

FORM PTO-1390 (REV. 12-2001)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER <b>514453-3916</b>
<b>TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371</b>			U.S. APPLICATION NO. (If known see 37 C.F.R. 1.5)  <b>10/070242</b>
INTERNATIONAL APPLICATION NO. <b>PCT/EP00/08518</b>	INTERNATIONAL FILING DATE <b>31 AUGUST 2000</b>	PRIORITY DATE CLAIMED <b>01 SEPTEMBER 1999</b>	
TITLE OF INVENTION <b>FIVE MEMBERED-RING COMPOUNDS AND UTILIZATION THEREOF IN LIQUID CRYSTAL MIXTURES</b>			
APPLICANT(S) FOR DO/EO/US <b>Barbara HORNING, Toshiaki NONAKA, Ayako OGAWA, Wolfgang SCHMIDT, Rainer WINGEN</b>			
<p>Applicants herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:</p> <ol style="list-style-type: none"> <li><input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li><input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li><input type="checkbox"/> This is an express request to promptly begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.</li> <li><input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (PCT Article 31).</li> <li><input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))             <ol style="list-style-type: none"> <li><input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).</li> <li><input type="checkbox"/> has been communicated by the International Bureau.</li> <li><input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ol> </li> <li><input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).             <ol style="list-style-type: none"> <li><input checked="" type="checkbox"/> is attached hereto.</li> <li><input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).</li> </ol> </li> <li><input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))             <ol style="list-style-type: none"> <li><input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).</li> <li><input type="checkbox"/> have been communicated by the International Bureau.</li> <li><input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</li> <li><input checked="" type="checkbox"/> have not been made and will not be made.</li> </ol> </li> <li><input type="checkbox"/> A English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</li> <li><input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</li> <li><input type="checkbox"/> An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</li> </ol> <p><b>Items 11 to 20 below concern document(s) or information included:</b></p> <ol style="list-style-type: none"> <li><input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</li> <li><input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</li> <li><input type="checkbox"/> A FIRST preliminary amendment.</li> <li><input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.</li> <li><input type="checkbox"/> A substitute specification.</li> <li><input type="checkbox"/> A change of power of attorney and/or address letter.</li> <li><input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.</li> <li><input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4).</li> <li><input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).</li> <li><input checked="" type="checkbox"/> Other items or information:  <div style="margin-left: 20px;"> PCT/IB/304, PCT/IPEA/402, 409, 416  PCT/ISA/210, 1 page Abstract </div> </li> </ol>			

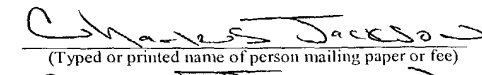
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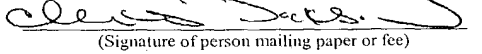
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U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.50) <b>10/070242</b>		INTERNATIONAL APPLICATION NO. PCT/EP00/08518		ATTORNEY'S DOCKET NO. 514453-3916	
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21. <input checked="" type="checkbox"/> The following fees are submitted				CALCULATIONS PTO USE ONLY	
<b>BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5):</b> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO..... \$1040.00  International preliminary examination fee (37 C.F.R. 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO..... \$890.00  International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO..... \$740.00  International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4)..... \$710.00  International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) ..... \$100.00					
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>					
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	
Total Claims	12 - 20 =	0	x \$18.00	\$ 0.00	
Independent Claims	3 - 3 =	0	x \$84.00	\$ 0.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)				+ \$280.00	
<b>TOTAL OF ABOVE CALCULATIONS =</b>				\$	
<input type="checkbox"/> Applicant claims small entity status. See 37 C.F.R. 1.27. The fees indicated above are reduced by 1/2.				+	
<b>SUBTOTAL =</b>				\$	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	
<b>TOTAL NATIONAL FEE =</b>				\$	
Fee for recording the enclosed assignments (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property				+	
<b>TOTAL FEES ENCLOSED =</b>				\$ 890.00	
				Amount to be refunded:	\$
				charged:	\$

a. ☒ A check in the amount of \$ 890.00 to cover the above fees is enclosed.

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**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR  
1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

**William F. Lawrence, Esq.**  
**Frommer Lawrence & Haug LLP**  
**745 Fifth Avenue**  
**New York, New York 10151**

Mark Lawrence, Reg. No. 37,514  
 SIGNATURE  
101  
 WILLIAM F. LAWRENCE  
 NAME  
 28,029  
 REGISTRATION NUMBER

**Dated: February 27, 2002**

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JC18 Rec'd PCT/PTO 27 FEB 2002

**CERTIFICATE OF MAILING – SEPARATE PAPER**

Attorney Docket No. : 514453-3916  
Serial No. : PCT/EP00/08518  
Applicant(s) : Barbara Hornung et al.

Date of Deposit February 27, 2002 via "Express Mail" # EV 001581103US

I hereby certify that a PCT, a Fee Transmittal Sheet, and related documents for the above-referenced application are being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 C.F.R. 1.10 on the date indicated above and is addressed to:

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00053432

"as originally filed"

**Five-membered ring compounds and their use in liquid-crystalline mixtures**

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Besides nematic and cholesteric liquid crystals, optically active, tilted smectic (ferroelectric) liquid crystals have also recently been used in commercial display devices.

Clark and Lagerwall have been able to show that the use of ferroelectric liquid crystals (FLCs) in very thin cells results in opto-electrical switching or display elements which have response times which are of up to 1000 times faster than conventional TN ("twisted nematic") cells (see, for example, EP-A 0 032 362). Owing to this and other favorable properties, for example the possibility of bistable switching and the virtually viewing angle-independent contrast, FLCs are basically highly suitable for areas of application such as computer displays.

For a more detailed discussion of the technical requirements of FLCs, reference is made to European Patent Application 97118671.3 and DE-A 197 48 432.

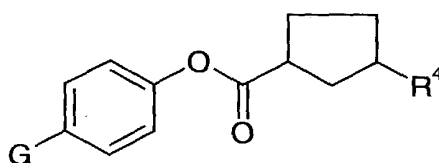
Thiophene derivatives have already been described for use in liquid-crystal mixtures, e.g. in EP-B 0 500 072. Some 3- or 4-fluorothiophenecarboxylic acids have also been described, e.g. in Tetrahedron Letters 1997, 38(6), 1049; Heterocycles 23, 1431 (1985); Synth.Comm. 24, 95 (1994). However, these latter documents do not indicate any suitability for use as a building block for liquid crystals.

JP-A 6306098 describes esters of furanacrylic acid having terminally polar phenols for use in nematic liquid-crystal mixtures.

JP-A 10-333113 describes 3,5-diarylisoxazoles for use in ferroelectric liquid-crystal mixtures, especially operated in inverse mode.

2,5-Diarylthiazoles for use in ferroelectric liquid-crystal mixtures are described,  
5 for example, in EP-B 0 439 170.

Cyclopentane derivatives have previously been described in general for use in liquid-crystal mixtures in US 4,873,019; however, this document does not suggest to the person skilled in the art that the compounds of the formula (II) encompassed  
10 by the general formula of this document are particularly suitable as components of chiral smectic liquid-crystal mixtures.



(II)

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in which

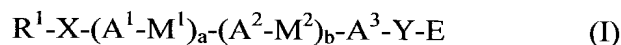
**R<sup>4</sup>** is as defined below

**G** is F or CN or trans-4-propyl-cyclohexyl or trans-4-butyl-cyclohexyl or an alkyl radical of 1 to 15 carbon atoms, in which one or more nonadjacent CH<sub>2</sub> groups  
20 may be replaced by -O-, -CO-, -OCO-, -O-CO-O-, -CHhalogen-, -CHCN- and / or -CH=CH-.

However, since the development, in particular of ferroelectric liquid-crystal mixtures, can in no way be regarded as complete, display manufacturers are  
25 interested in a wide variety of components for mixtures, partly because only the interaction of the liquid-crystalline mixtures with the individual components of the display device or of the cells (for example the alignment layer) allows conclusions to be drawn on the quality of the liquid-crystalline mixtures.

It has now been found that five-membered ring compounds of the formula (I), even when admixed in small amounts, have a favorable effect on the properties of liquid-crystal mixtures, in particular chiral smectic mixtures, for example regarding the dielectric anisotropy and/or the melting point, but also regarding the switching behavior, the tilt angle values and the temperature dependence of the tilt angle.

The invention therefore provides five-membered ring compounds of the formula (I),



where the symbols and indices have the following meanings:

**E** is a radical  $T-Z-R^2$  containing a five-membered ring, where:

- (i) **T** is undirected and is  
4-fluorothiophene-2,5-diyl, 3-fluorothiophene-2,5-diyl,  
3-fluorothiophene-2,4-diyl or 5-fluorothiophene-2,4-diyl
- Z** is a single bond or -O-
- R<sup>2</sup>** is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 20 carbon atoms, where one nonterminal CH<sub>2</sub> group may be replaced by -O- or -OC(=O)- or -C(=O)O- and/or one or more H atoms may be replaced by F, with the provisos that
- a) the -CH<sub>2</sub>- group nearest to the thiophene cannot be replaced by -O- when Z is -O-
- b) R<sup>2</sup> can only be hydrogen when Z is a single bond,

- (ii) **T** is furan-2,5-diyl or furan-2,4-diyl
- Z** is a single bond or -O-

- 5           **R<sup>2</sup>**    is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 20 carbon atoms, where one nonterminal CH<sub>2</sub> group nonadjacent to furan may be replaced by -O- or -OC(=O)- or -C(=O)O- and/or one or more H atoms may be replaced by F,
- (iii)   **T**    is undirected and is isoxazole-3,5-diyl  
         **Z**    is a single bond or -O-
- 10           **R<sup>2</sup>**    is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 20 carbon atoms, where one nonterminal CH<sub>2</sub> group may be replaced by -O- or -OC(=O)- or -C(=O)O- and/or one or more H atoms may be replaced by F, with the provisos that
- 15           a) the -CH<sub>2</sub>- group nearest to the isoxazole cannot be replaced by -O- when Z is -O-  
             b) **R<sup>2</sup>** can only be hydrogen when Z is a single bond,
- (iv)    **T**    is undirected and is thiazole-2,5-diyl or thiazole-2,4-diyl  
20           **Z**    is a single bond  
             **R<sup>2</sup>**    is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 20 carbon atoms, where one nonterminal CH<sub>2</sub> group may be replaced by -O- or -OC(=O)- or -C(=O)O- and/or one or more H atoms may be
- 25           replaced by F,
- (v)    **T**    is cyclopentane-1,3-diyl  
         **Z**    is a single bond or -O-  
             **R<sup>2</sup>**    is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 20 carbon atoms, where one nonterminal CH<sub>2</sub> group may be replaced by -O- or
- 30

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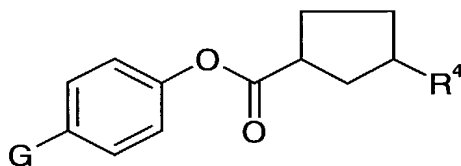
-OC(=O)- or -C(=O)O- and/or one or more H atoms may be replaced by F, with the provisos that

a) the -CH<sub>2</sub>- group nearest to the cyclopentane cannot be replaced by -O- when Z is -O-

5

b) R<sup>2</sup> can only be hydrogen when Z is a single bond,

with the exception of compounds of the formula (II)



(II)

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in which

**R<sup>4</sup>** is as defined for **R<sup>2</sup>**

**G** is trans-4-propyl-cyclohexyl or trans-4-butyl-cyclohexyl or an alkyl group of 1 to 15 carbon atoms, in which, in addition, one or more nonadjacent CH<sub>2</sub> groups may be replaced by -O-, -CO-, -OCO-, -O-CO-O-, -CHhalogen-, -CHCN- and/or -CH=CH- or is F, CN,

15

(vi) **T** is cyclopentane-1,3-diyl, in which one -CH<sub>2</sub>CH<sub>2</sub>- or -CH<sub>2</sub>CH- group is replaced by a -CH=CH- or CH=C- group respectively

20

**Z** is a single bond

**R<sup>2</sup>** is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 20 carbon atoms, where one nonterminal CH<sub>2</sub> group may be replaced by -O- or -OC(=O)- or -C(=O)O- and/or one or more H atoms may be replaced by F, with the proviso that the -CH<sub>2</sub>- group nearest to the cyclopentene cannot be replaced and where

25

**Y** cannot be -CH<sub>2</sub>-CH<sub>2</sub>-,



**R<sup>1</sup>** is hydrogen or a straight-chain or branched C<sub>1-20</sub>-alkyl or C<sub>2-20</sub>-alkenyl radical (with or without asymmetric carbon atoms), where

- a) one or two nonterminal CH<sub>2</sub> groups may be replaced, independently of one another, by -O- or -C(=O)-, with the proviso that two adjacent CH<sub>2</sub> groups cannot be replaced in the same way, and/or
- b) one CH<sub>2</sub> group may be replaced by -C≡C-, and/or
- c) one CH<sub>2</sub> group may be replaced by -Si(CH<sub>3</sub>)<sub>2</sub>-, cyclopropane-1,2-diyl, cyclobutane-1,3-diyl, cyclopentane-1,4-diyl, bicyclo[1.1.1]pentane-1,3-diyl or cyclohexane-1,4-diyl, and/or
- d) one or more H atoms may be replaced by F and/or CN,
- e) in the case of a branched alkyl radical containing asymmetric carbon atoms, the asymmetric carbon atoms have -CH<sub>3</sub>, -OCH<sub>3</sub>, -CF<sub>3</sub>, F, CN and/or Cl as substituents or are incorporated into a 3- to 7-membered ring, in which, in addition, one or two non-adjacent CH<sub>2</sub> groups may be replaced by -O- and one CH<sub>2</sub> group non-adjacent to these groups may be replaced by -OC(=O)-;

**X** is a single bond, -O-, OC(=O)-, -C(=O)O- or -OC(=O)O-

**Y** is -OC(=O)-, -OCH<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>-

**A<sup>1</sup>, A<sup>2</sup>, A<sup>3</sup>** are each, independently of one another,

phenylene-1,4-diyl, unsubstituted or monosubstituted or disubstituted by CN or F, phenylene-1,3-diyl, unsubstituted or monosubstituted or disubstituted by CN or F, cyclohexane-1,4-diyl, in which one or two H atoms may be replaced by CN and/or CH<sub>3</sub> and/or F, 1-cyclohexene-1,4-diyl, in which one H atom may be replaced by F, 1-alkyl-1-silacyclohexane-1,4-diyl, pyridine-2,5-diyl, unsubstituted or monosubstituted by F, pyrimidine-2,5-diyl, unsubstituted or monosubstituted by F, cyclopentane-2,5-diyl or thiophene-2,5-diyl;

$M^1, M^2$  are undirected and are each, independently of one another,

-OC(=O)-, -OCH<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>-, -OC(=O)CH<sub>2</sub>CH<sub>2</sub>-, -OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-,  
-C≡C-, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>- or a single bond;

5 **a, b** are each, independently of one another, 0 or 1.

The term "terminal" means, for example in R<sup>1</sup>, the CH<sub>2</sub> groups connected to X or to H. The term "undirected" means that incorporation of the group in the form of its mirror image is possible.

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The five-membered ring compounds of the formula (I) are fluorinated thiophene derivatives (i), furan derivatives (ii), isoxazole derivatives (iii), thiazole derivatives (iv), cyclopentane derivatives (v) or cyclopentene derivatives (vi).

15 In one embodiment of the invention, one or more of the following provisos apply:

For thiophene derivatives (i), A<sup>1</sup>, A<sup>2</sup>, A<sup>3</sup> are not cyclopentane-2,5-diyl.

For furan derivatives, A<sup>1</sup>, A<sup>2</sup>, A<sup>3</sup> are not cyclopentane-2,5-diyl.

For isoxazole derivatives, A<sup>1</sup>, A<sup>2</sup>, A<sup>3</sup> are not cyclopentane-2,5-diyl.

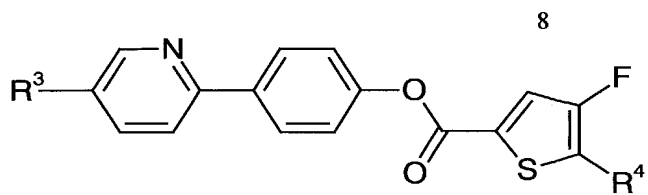
20 For thiazole derivatives, A<sup>1</sup>, A<sup>2</sup>, A<sup>3</sup> are not cyclopentane-2,5-diyl.

For cyclopentane derivatives, A<sup>1</sup>, A<sup>2</sup>, A<sup>3</sup> are not thiophene-2,5-diyl.

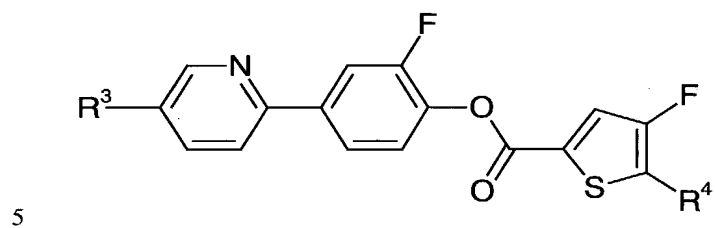
For cyclopentene derivatives, cyclopentane-1,4-diyl is replaced by cyclopentane-1,3-diyl for R<sup>1</sup> in proviso c).

25 **Fluorinated thiophene derivatives**

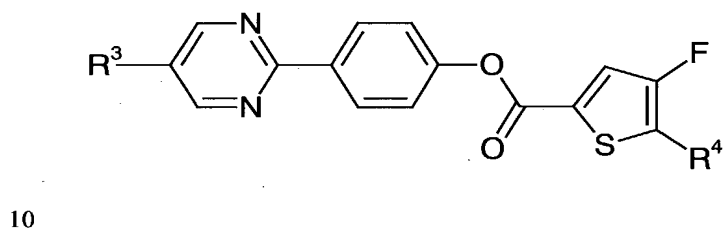
Preferred thiophene derivatives (i) are the following compounds of the formulae (I-1) to (I-33)



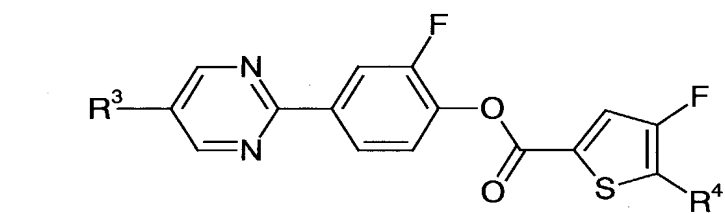
(I-1)



(I-2)

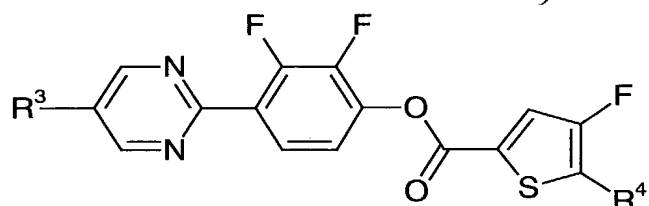


(I-3)



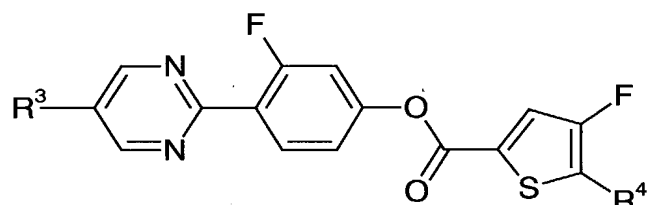
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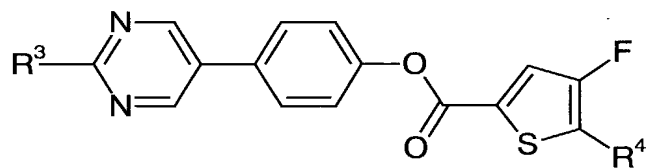
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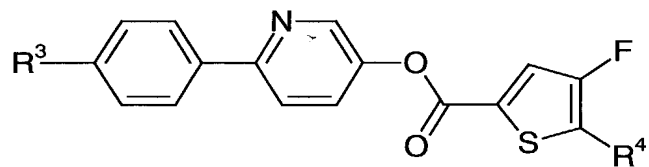
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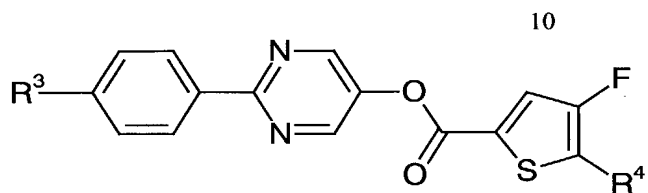


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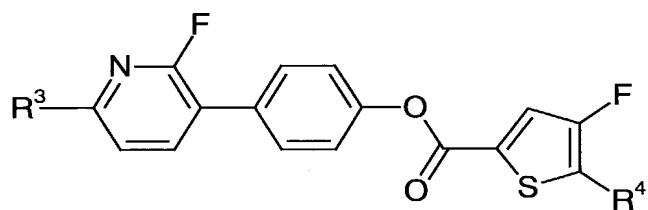
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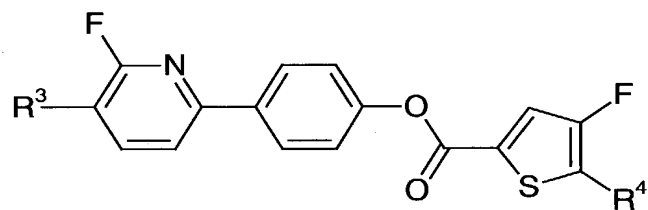
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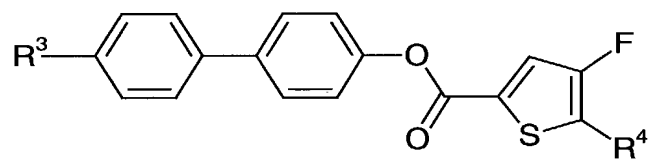
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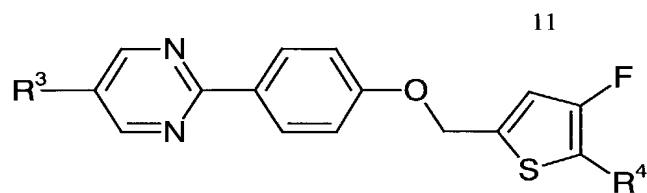
(I-10)



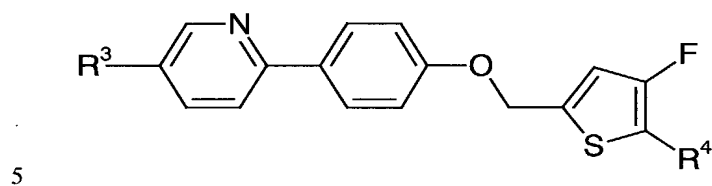
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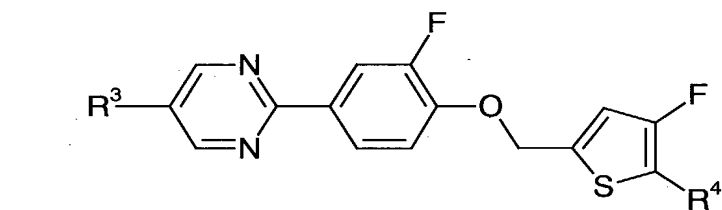
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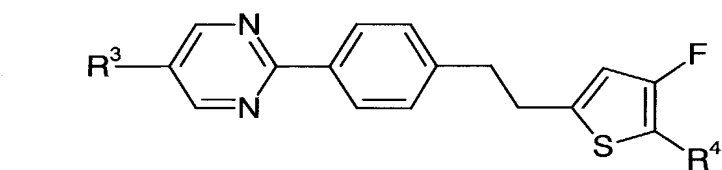
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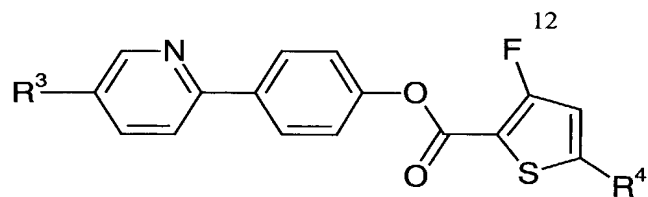
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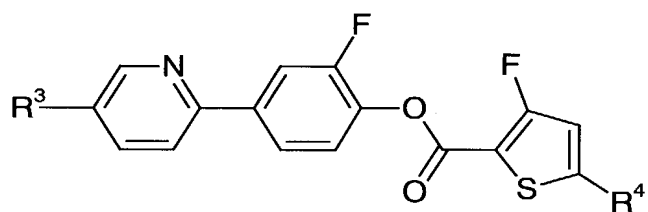
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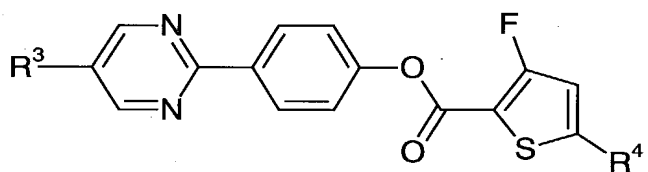
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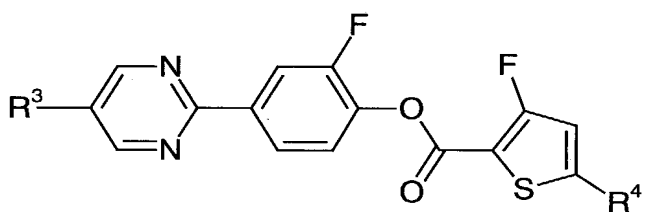
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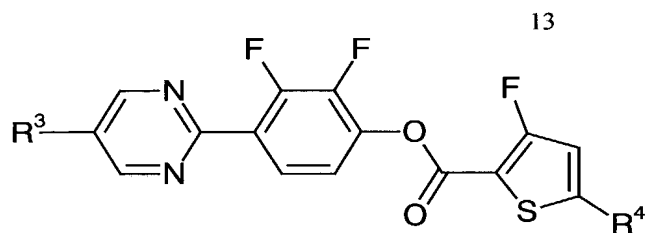
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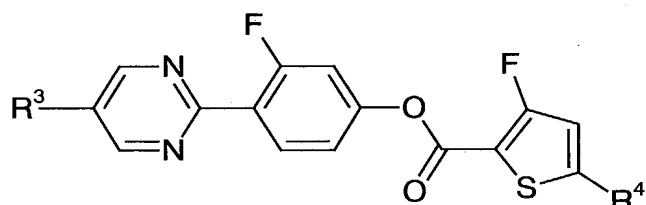
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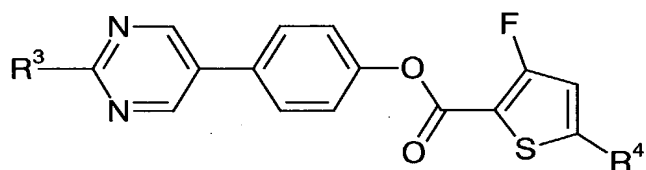
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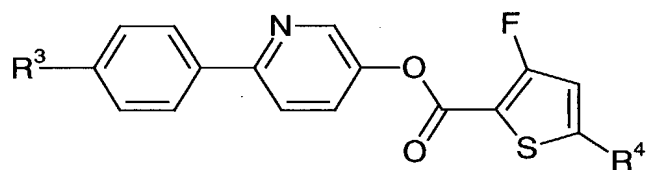
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(I-23)

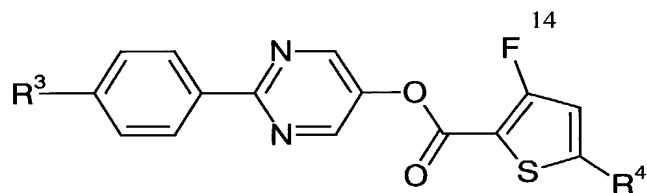


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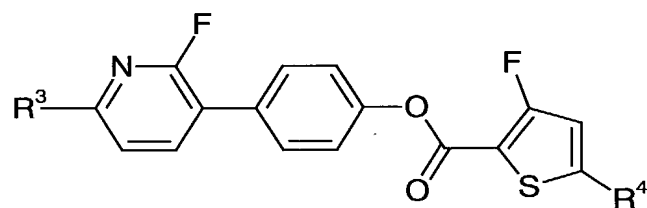


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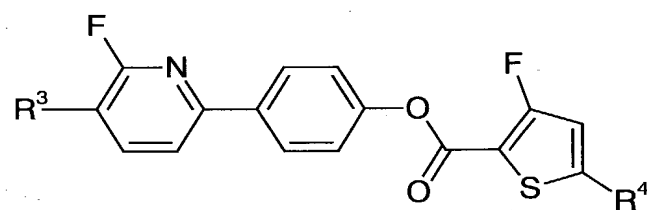


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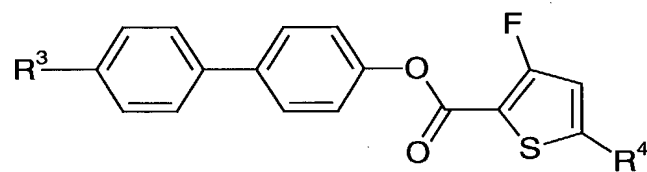
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(I-27)



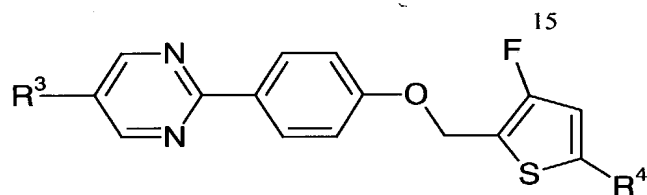
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(I-28)

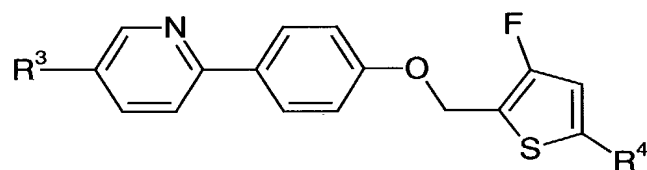


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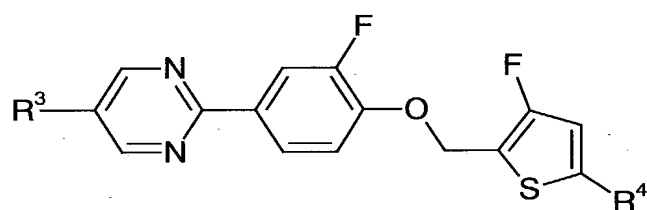
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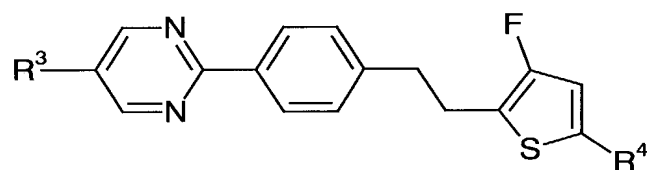
(I-30)



(I-31)



(I-32)



(I-33)

in which:

$R^3$  is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 16 carbon atoms, where one nonterminal

16

CH<sub>2</sub> group may, in addition, be replaced by -O- or, undirected, by -OC(=O)- and one or more H atoms may be replaced by F;

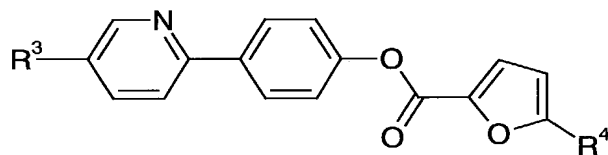
**R<sup>4</sup>** is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 16 carbon atoms.

Particular preference is given to compounds of the formulae (I), in particular (I-1) to (I-33), in which **R<sup>3</sup>** and **R<sup>4</sup>** are each, independently of one another, a straight-chain alkyl radical having 2 to 16 carbon atoms.

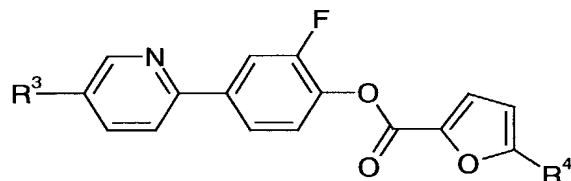
Particular preference is likewise given to compounds of the formula (I), in particular (I-1) to (I-33), in which **R<sup>3</sup>** is a straight-chain alkoxy radical having 2 to 12 carbon atoms and **R<sup>4</sup>** is hydrogen or a straight-chain alkyl radical having 2 to 12 carbon atoms.

### Furan derivatives

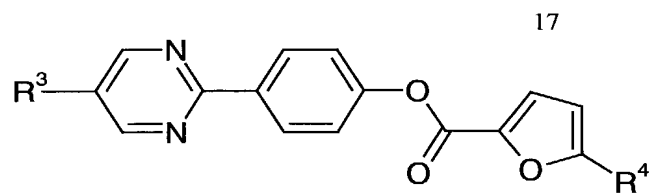
Preferred furan derivatives (ii) are the following compounds of the formulae (I-1) to (I-16)



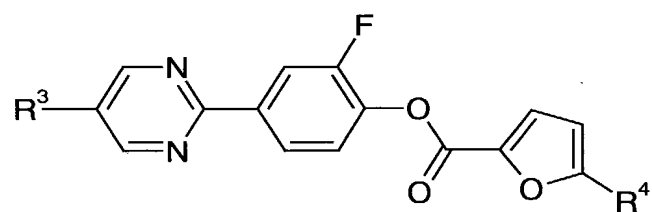
(I-1)



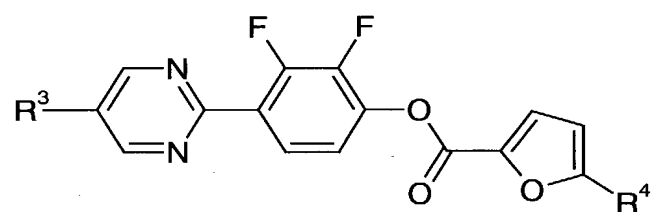
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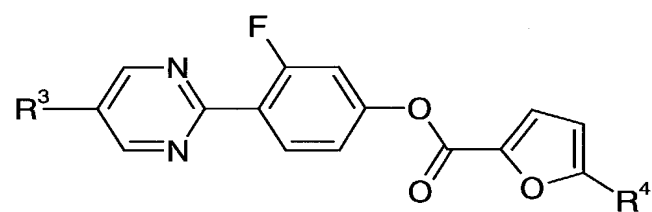
(I-3)



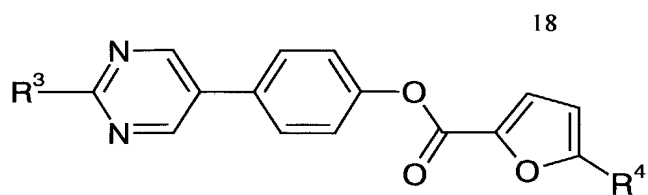
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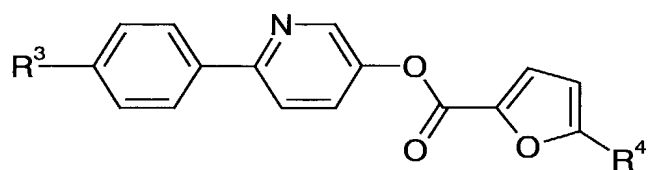
(I-5)



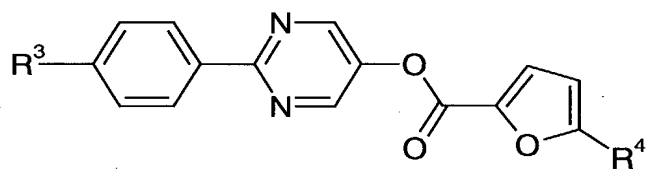
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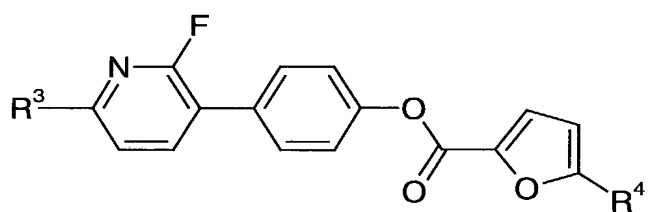
(I-7)



(I-8)

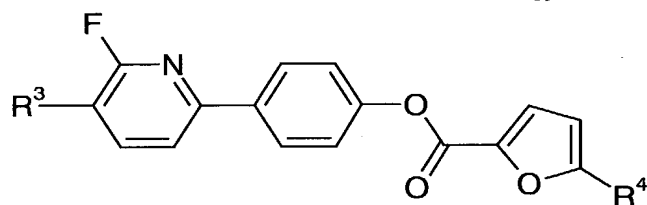


(I-9)

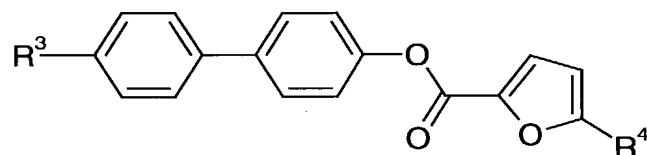


(I-10)

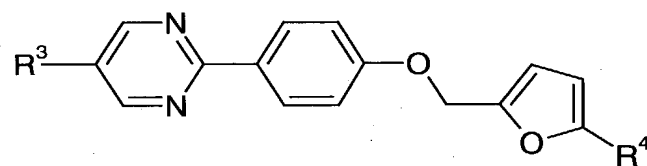
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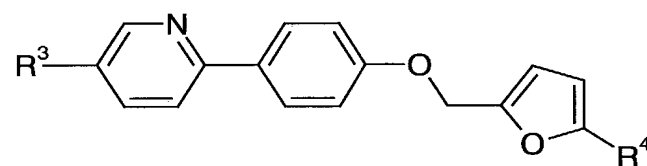
(I-11)



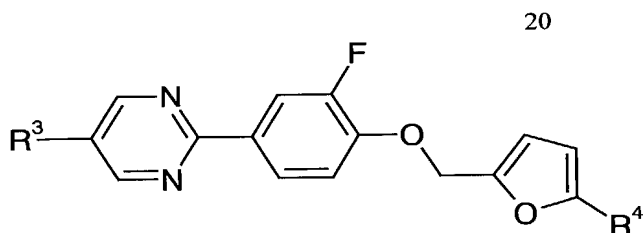
(I-12)



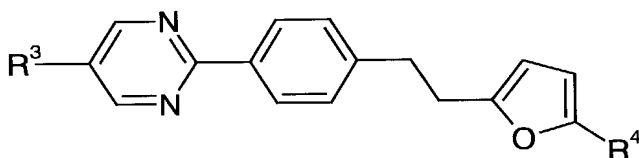
(I-13)



(I-14)



(I-15)



(I-16)

in which:

- 10 **R³** is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 16 carbon atoms, where one nonterminal CH<sub>2</sub> group may be replaced by -O- or undirected -OC(=O)- and one or more H atoms may be replaced by F;
- 15 **R⁴** is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 16 carbon atoms.

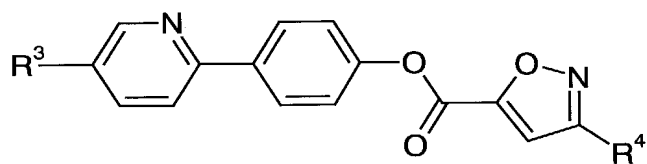
Particular preference is given to compounds of the formulae (I), in particular (I-1) to (I-16), in which **R³** and **R⁴** are each, independently of one another, a straight-chain alkyl radical having 2 to 16 carbon atoms.

Particular preference is likewise given to compounds of the formulae (I), in particular (I-1) to (I-16), in which **R³** is a straight-chain alkoxy radical having 2 to 12 carbon atoms and **R⁴** is hydrogen or a straight-chain alkyl radical having 2 to 12 carbon atoms.

**Isoxazole derivatives**

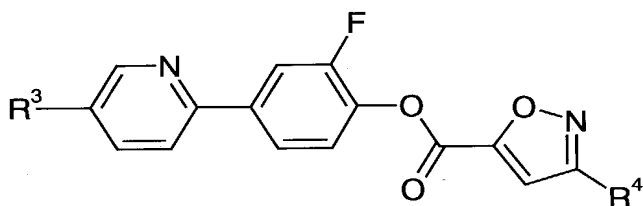
Preferred isoxazole derivatives (iii) are the following compounds of the formulae (I-1) to (I-15)

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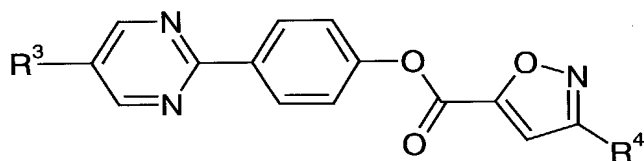
(I-1)

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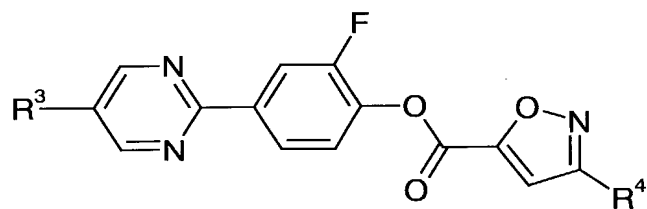
(I-2)

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(I-3)

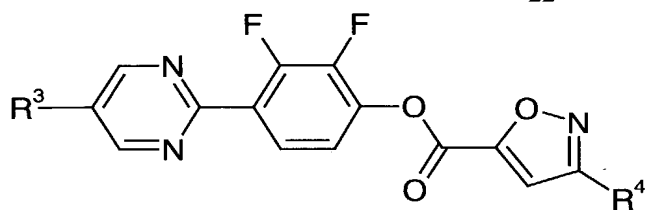
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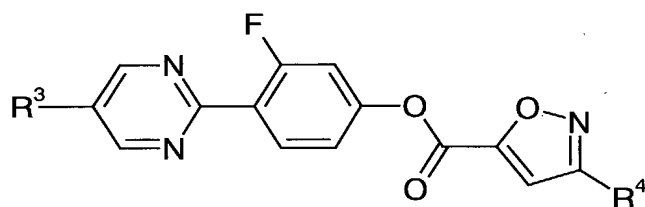
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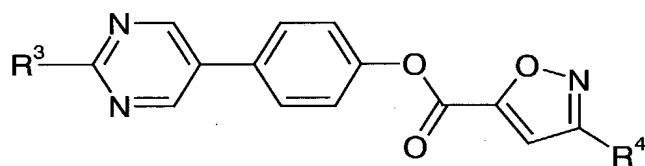
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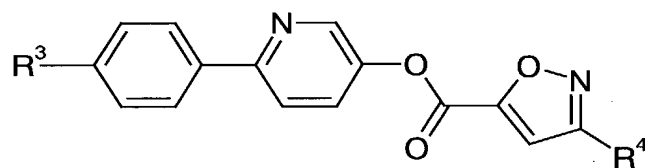
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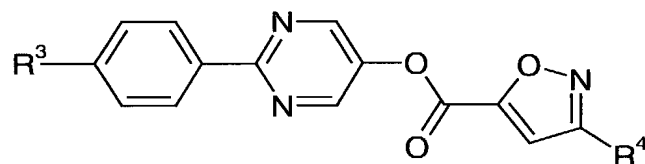
(I-6)



(I-7)

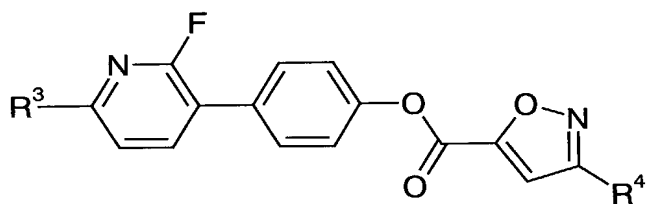


(I-8)



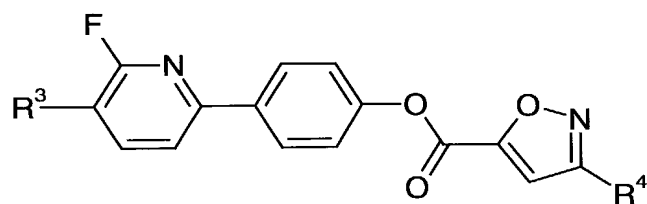
(I-9)

23



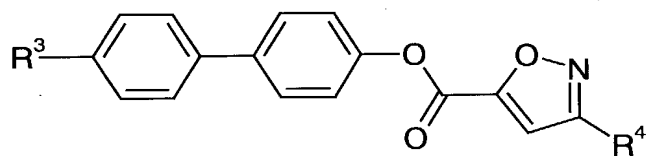
(I-10)

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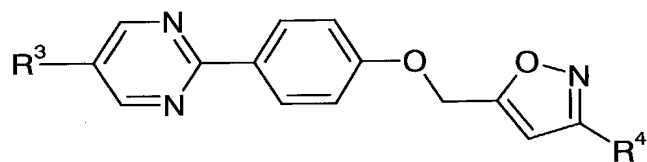
(I-11)

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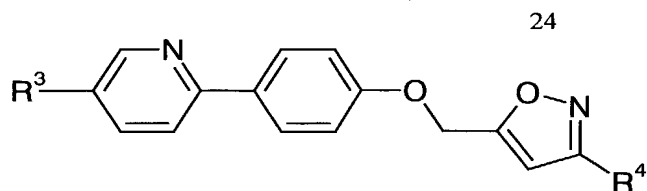


(I-12)

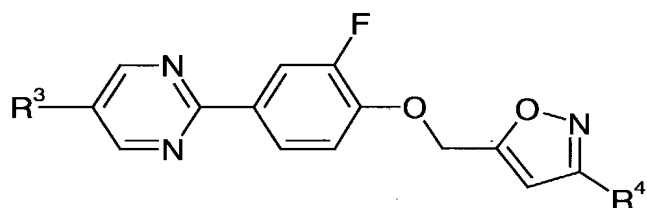
15



(I-13)



(I-14)



(I-15)

in which:

- 10 **R<sup>3</sup>** is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 16 carbon atoms, where one nonterminal CH<sub>2</sub> group may be replaced by -O- or undirected -OC(=O)- and one or more H atoms may be replaced by F;
- 15 **R<sup>4</sup>** is hydrogen or a straight-chain or branched alkyl or alkyloxy radical (with or without asymmetric carbon atoms) having 1 to 16 carbon atoms.

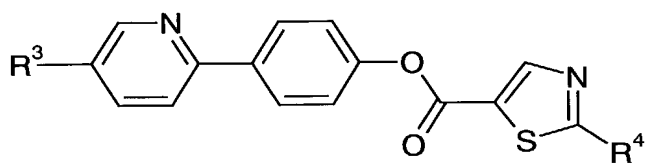
Particular preference is given to compounds of the formula (I), in particular (I-1) to (I-16), in which **R<sup>3</sup>** is a straight-chain alkyl radical having 2 to 16 carbon atoms and **R<sup>4</sup>** is a straight-chain alkyl or alkyloxy radical having 1 to 16 carbon atoms.

Particular preference is likewise given to compounds of the formula (I), in particular (I-1) to (I-16), in which **R<sup>3</sup>** is a straight-chain alkoxy radical having 2 to 12 carbon atoms and **R<sup>4</sup>** is a straight-chain alkyl or alkyloxy radical having 1 to 12 carbon atoms.

**Thiazole derivatives**

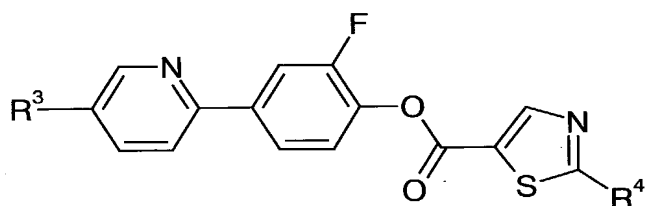
Preferred thiazole derivatives (iv) are the following compounds of the formulae (I-1) to (I-15)

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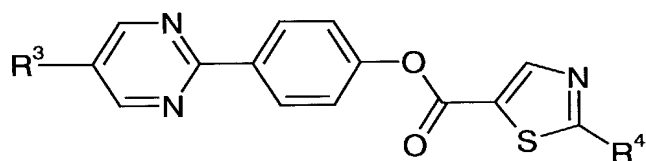
(I-1)

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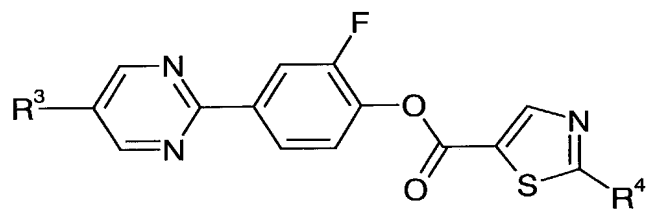
(I-2)

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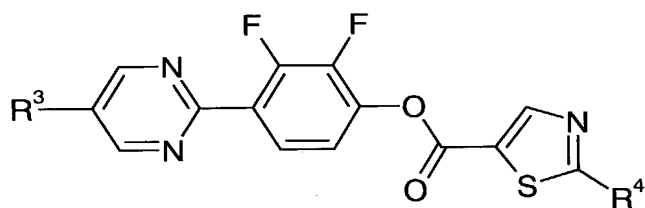
(I-3)

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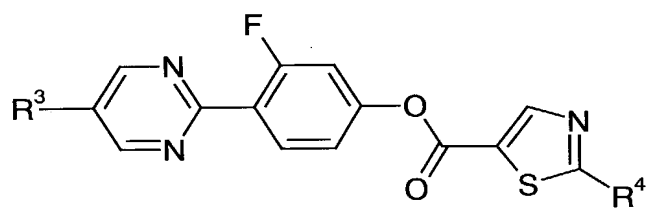
(I-4)

26



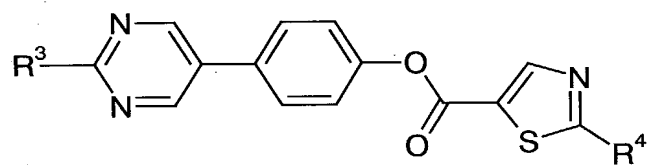
(I-5)

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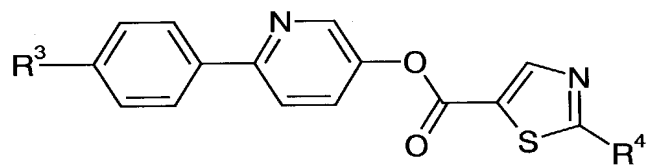
(I-6)

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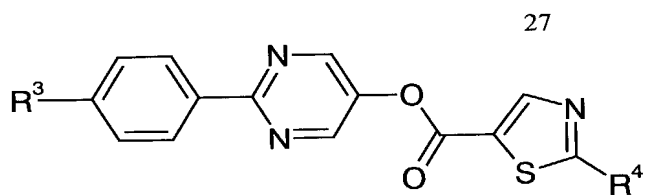


(I-7)

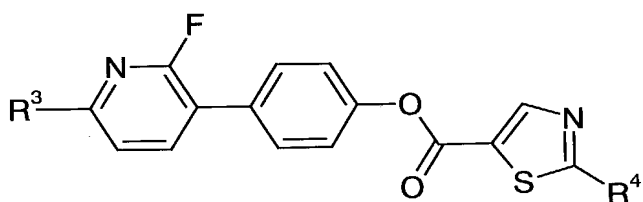
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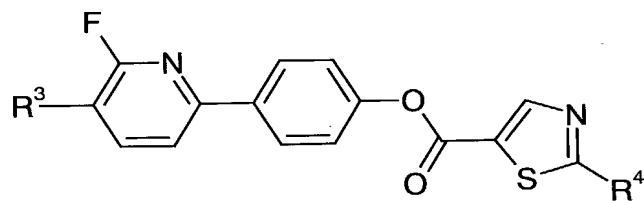
(I-8)



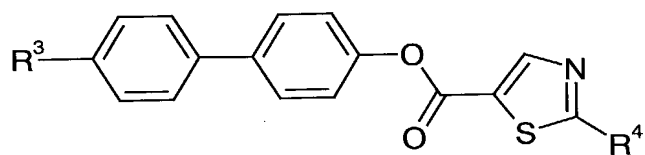
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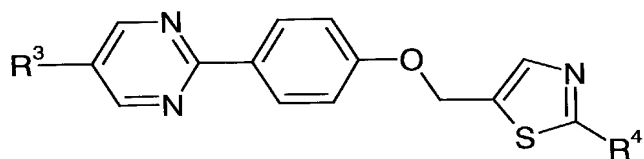
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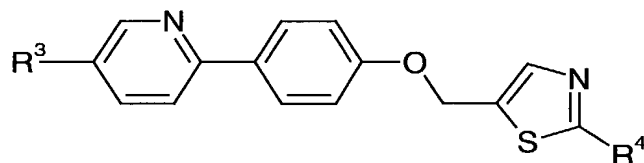
(I-11)



(I-12)

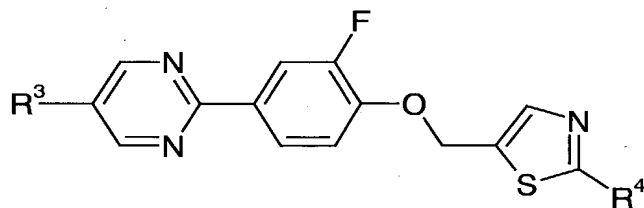


(I-13)



(I-14)

5



(I-15)

10 in which:

**R<sup>3</sup>** is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 16 carbon atoms, where one nonterminal CH<sub>2</sub> group may be replaced by -O- or undirected -OC(=O)- and one or more H atoms may be replaced by F;

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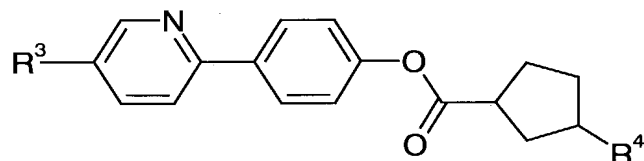
**R<sup>4</sup>** is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 16 carbon atoms.

Particular preference is given to compounds of the formulae (I), in particular (I-1) to (I-15), in which **R<sup>3</sup>** is a straight-chain alkyl radical having 2 to 16 carbon atoms and **R<sup>4</sup>** is a straight-chain alkyl radical having 1 to 16 carbon atoms.

Particular preference is likewise given to compounds of the formulae (I), in particular (I-1) to (I-15), in which **R<sup>3</sup>** is a straight-chain alkoxy radical having 2 to 12 carbon atoms and **R<sup>4</sup>** is a straight-chain alkyl radical having 1 to 12 carbon atoms.

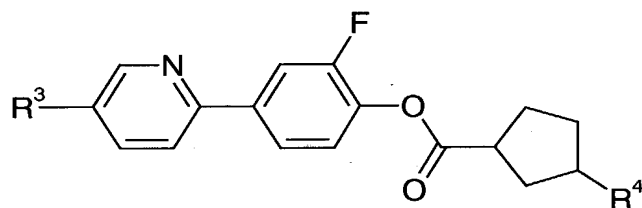
**Cyclopentane derivatives**

Preferred cyclopentane derivatives (v) are the following compounds of the  
5 formulae (I-1) to (I-16)



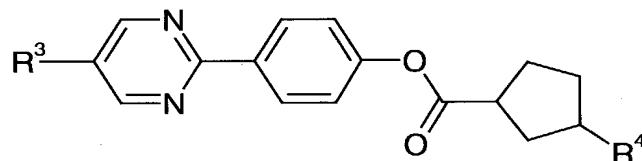
(I-1)

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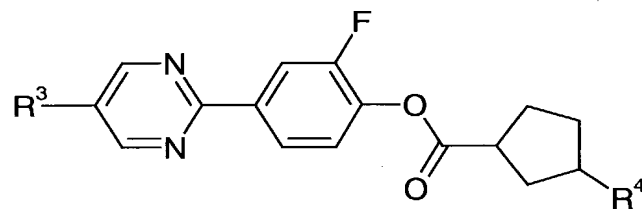
(I-2)

15



(I-3)

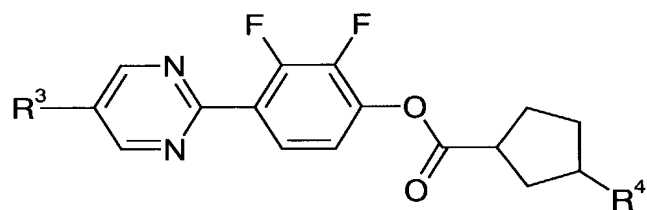
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(I-4)

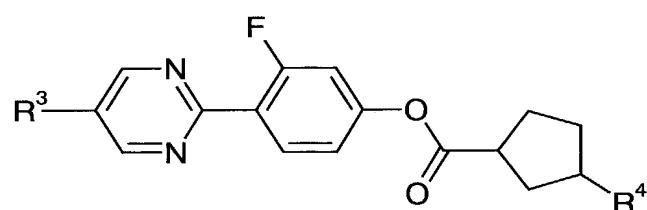


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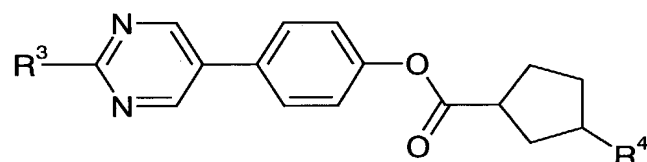
(I-5)

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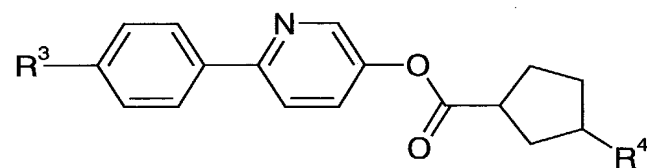
(I-6)

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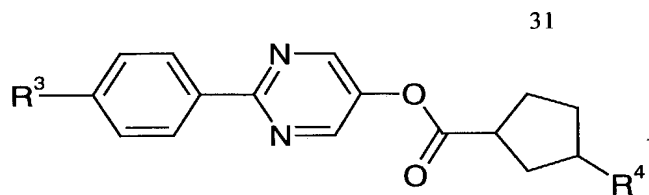


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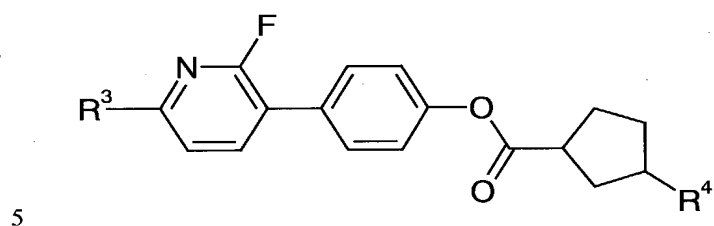
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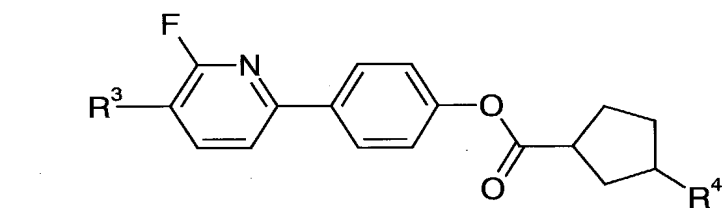
(I-8)



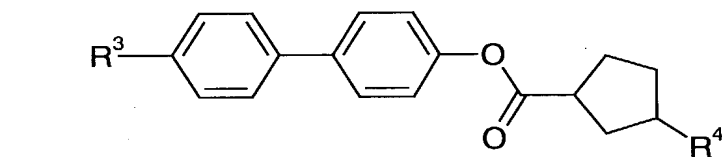
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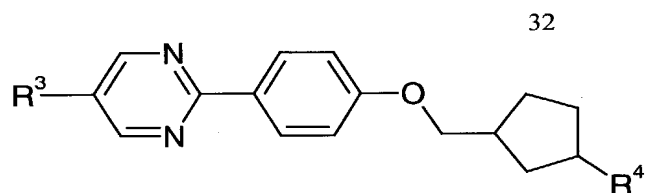
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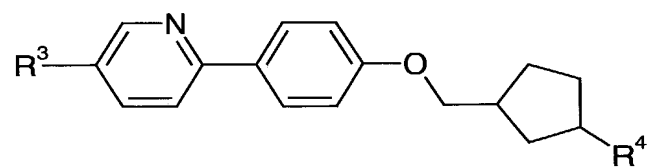
(I-11)



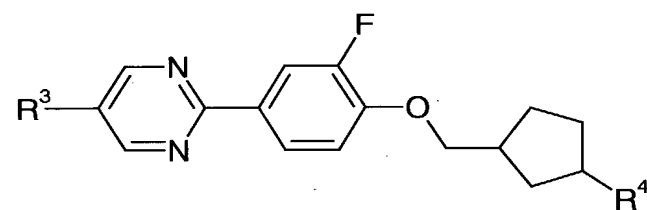
(I-12)



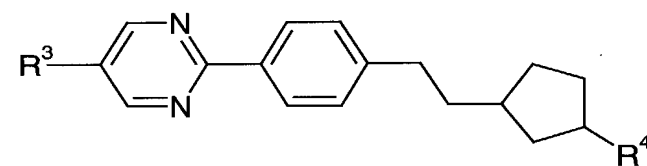
(I-13)



(I-14)



(I-15)



(I-16)

in which:

$R^3$  is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 16 carbon atoms, where one nonterminal  
20  $CH_2$  group may be replaced by  $-O-$  or undirected  $-OC(=O)-$  and one or more H atoms may be replaced by F;

$R^4$  is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 16 carbon atoms.

- 5 Particular preference is given to compounds of the formulae (I), in particular (I-1) to (I-16), in which  $R^3$  and  $R^4$  are each, independently of one another, a straight-chain alkyl radical having 2 to 16 carbon atoms.

10 Particular preference is likewise given to compounds of the formula (I), in particular (I-1) to (I-16), in which  $R^3$  is a straight-chain alkoxy radical having 2 to 12 carbon atoms and  $R^4$  is hydrogen or a straight-chain alkyl radical having 2 to 12 carbon atoms.

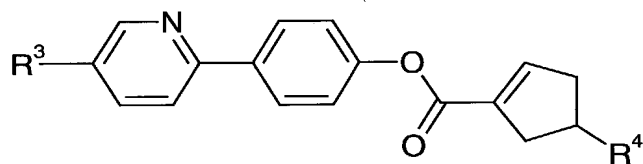
#### Cyclopentene derivatives

15

T is preferably

1-cyclopentene-1,3-diyl, 1-cyclopentene-1,4-diyl or 3-cyclopentene-1,3-diyl.

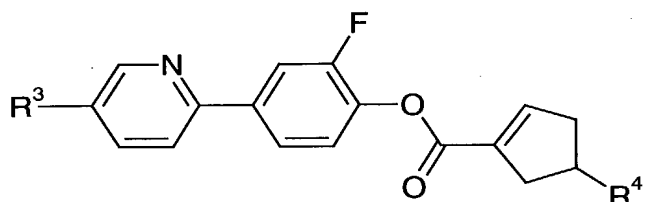
20 Preferred cyclopentene derivatives (vi) are the following compounds of the formulae (I-1) to (I-45)



(I-1)

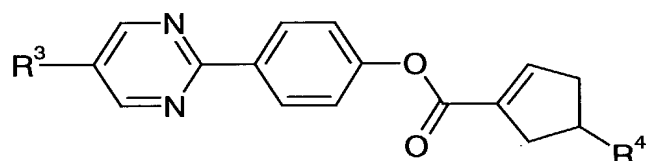
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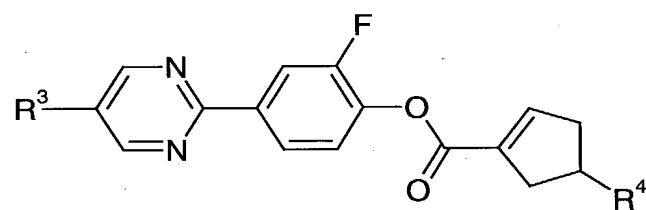
(I-2)

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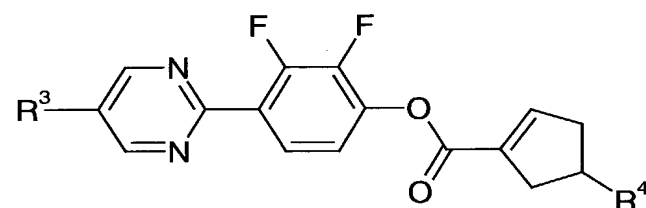
(I-3)

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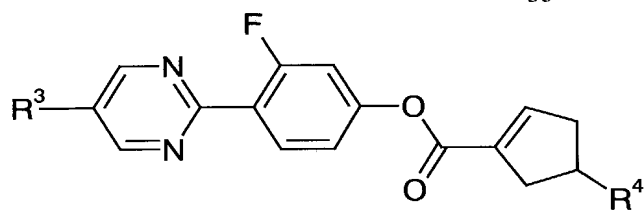
(I-4)

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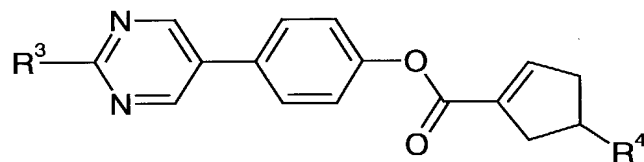


(I-5)

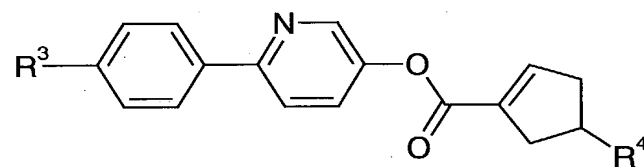
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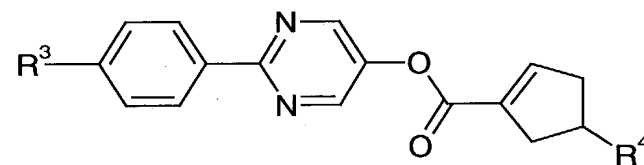
(I-6)



(I-7)

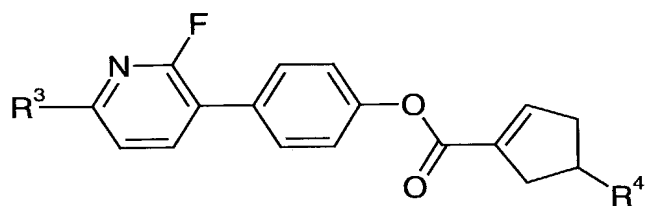


(I-8)

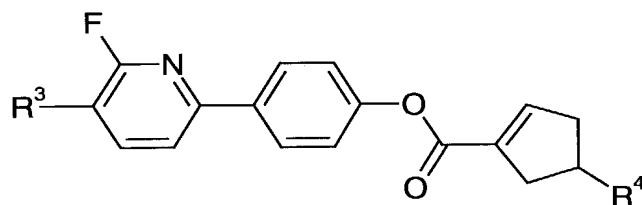


(I-9)

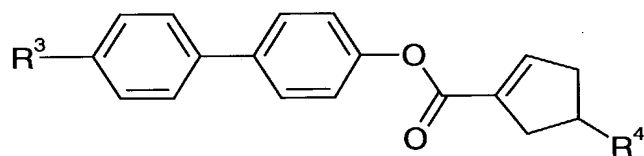
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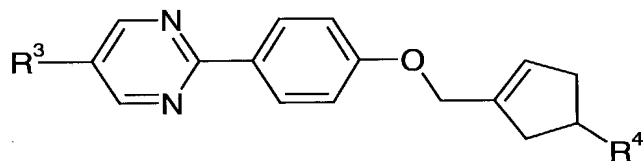
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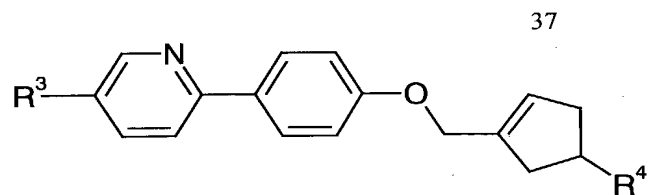
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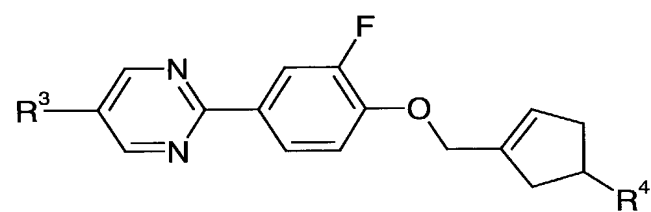
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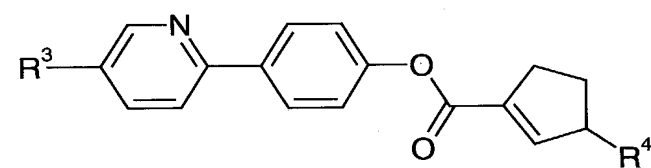
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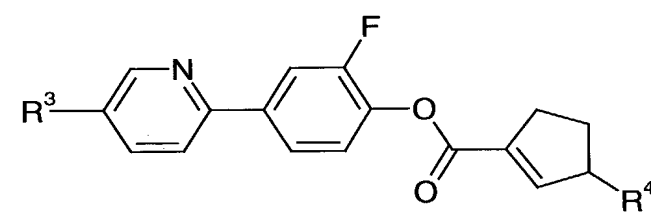
(I-14)



(I-15)

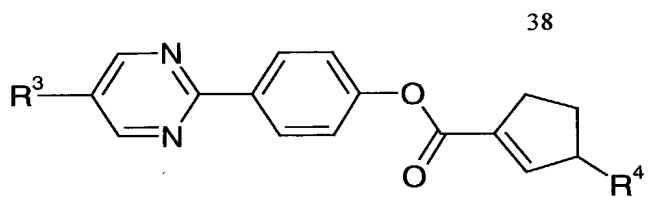


(I-16)

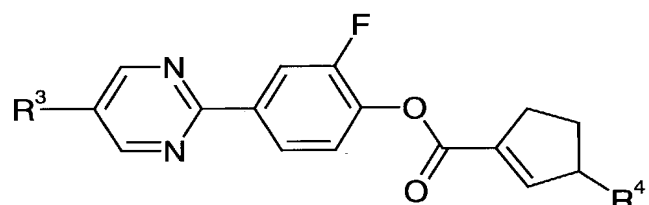


(I-17)

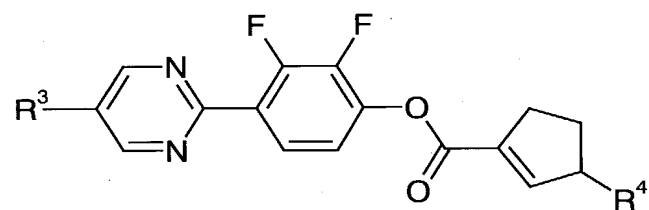




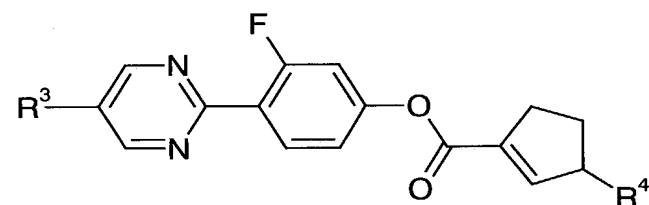
(I-18)



(I-19)

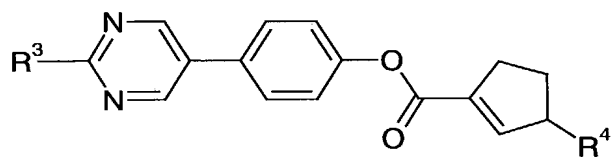


(I-20)



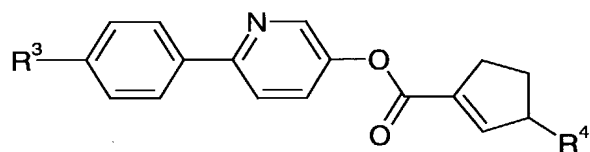
(I-21)

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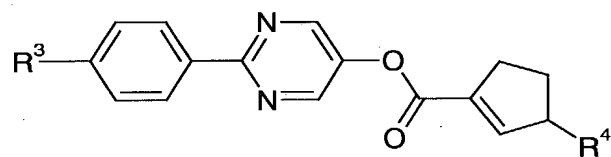
(I-22)

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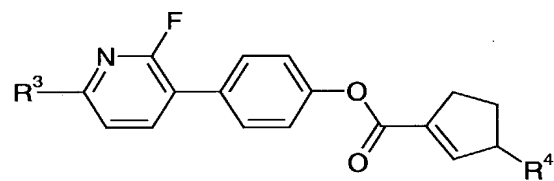
(I-23)

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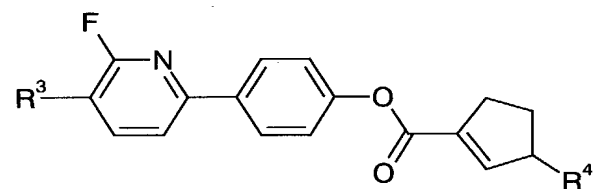


(I-24)

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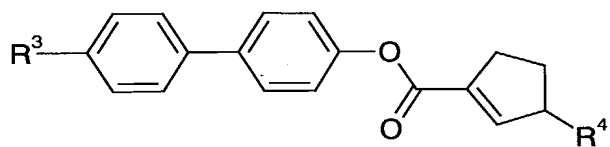


(I-25)

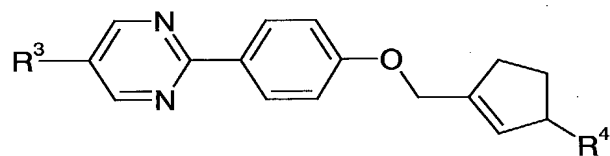


(I-26)

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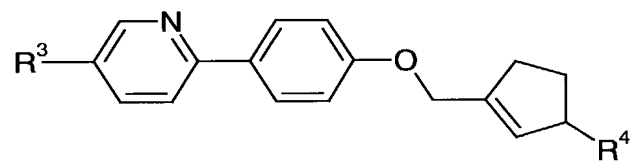


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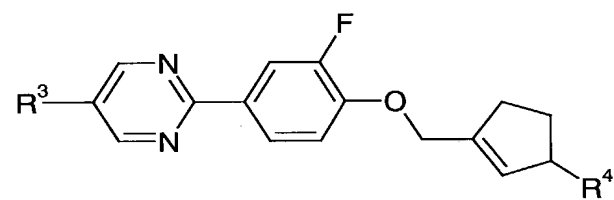
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(I-28)



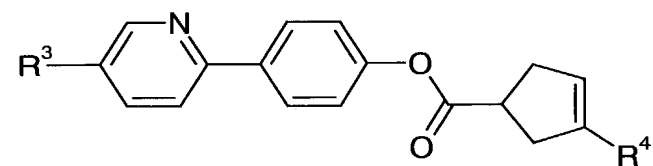
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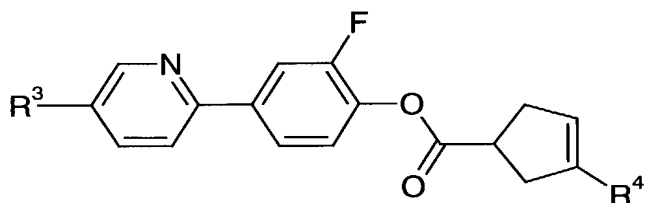
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(I-30)



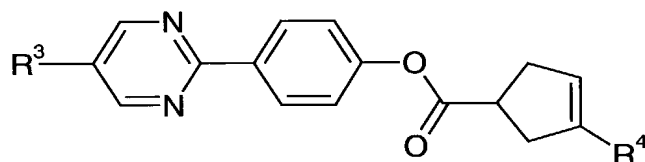
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41



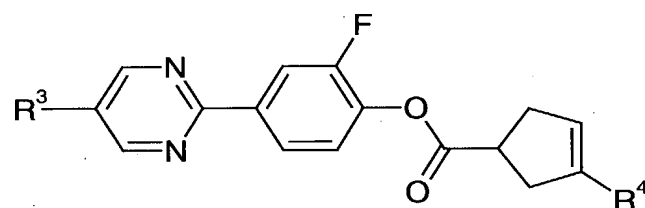
(I-32)

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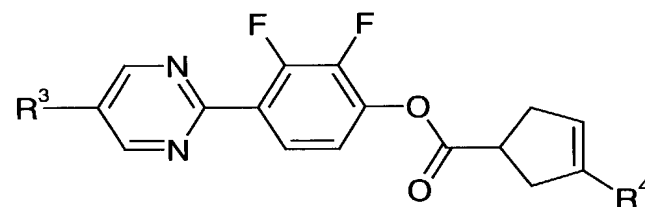
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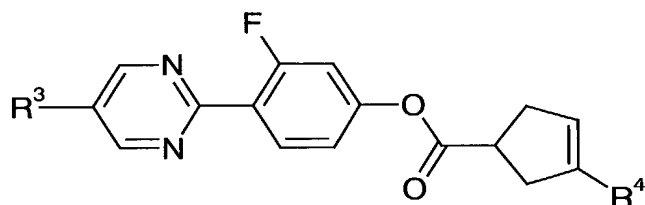
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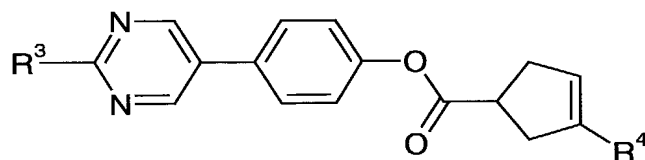


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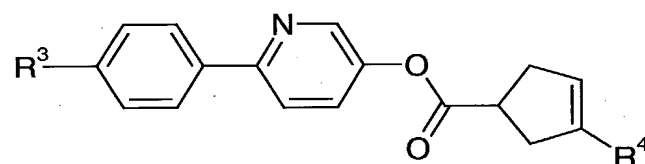
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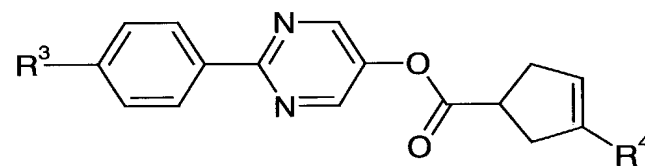
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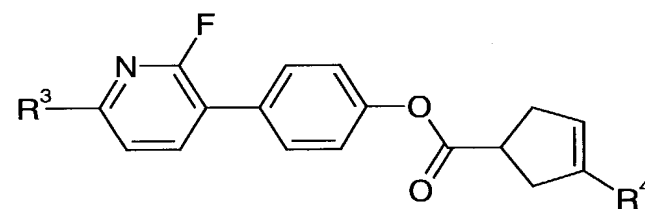
(I-37)



(I-38)

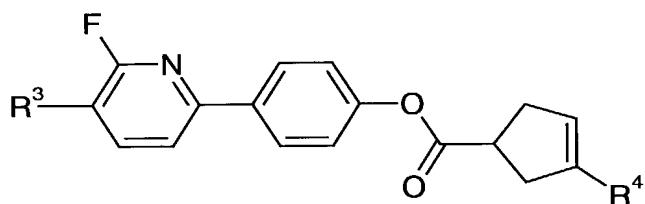


(I-39)



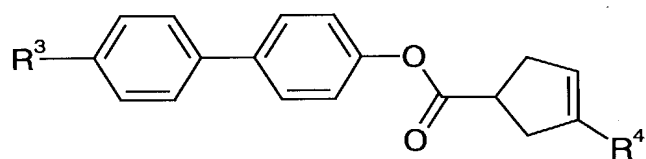
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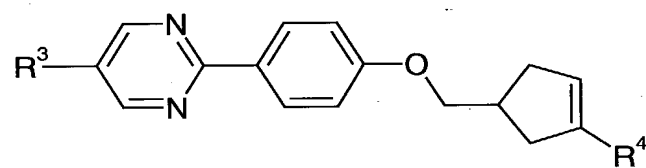
(I-41)

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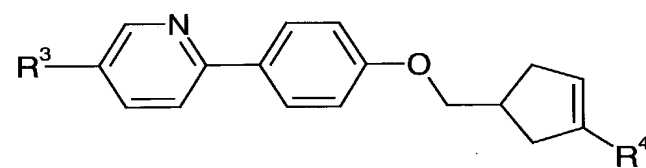
(I-42)

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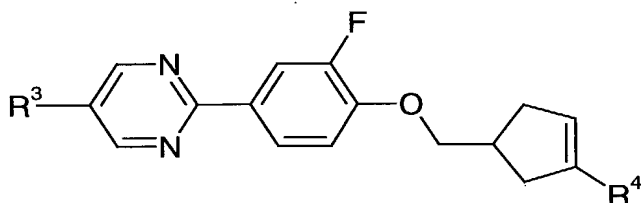
(I-43)

15



(I-44)

44



(I-45)

5 in which:

$R^3$  is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 16 carbon atoms, where one nonterminal  $CH_2$  group may, in addition, be replaced by  $-O-$  or, undirected, by  $-OC(=O)-$  and one or more H atoms may be replaced by F;

10

$R^4$  is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 16 carbon atoms.

Particular preference is given to compounds of the formulae (I), in particular (I-1) to (I-45), in which  $R^3$  and  $R^4$  are each, independently of one another, a straight-chain alkyl radical having 1 to 16 carbon atoms.

Particular preference is likewise given to compounds of the formula (I), in particular (I-1) to (I-45), in which  $R^3$  is a straight-chain alkoxy radical having 2 to 12 carbon atoms and  $R^4$  is hydrogen or a straight-chain alkyl radical having 1 to 12 carbon atoms.

Particular preference is likewise given to compounds of the formula (I), in particular (I-1) to (I-45), in which  $R^3$  is a branched alkyl or alkyloxy radical having 2 to 12 carbon atoms and  $R^4$  is hydrogen or a straight-chain alkyl radical having 1 to 12 carbon atoms.

Of the compounds of the formula (I) which are to be used as optically active components (dopants) in liquid-crystal mixtures, preference is given to those in

which the alkyl group contains the asymmetric carbon atoms in the form of at least one of the following groups:

- a)  $-C^*H(CH_3)C_mH_{2m+1}$ , where m has a value of from 2 to 8
- b)  $-OC^*H(CH_3)C_mH_{2m+1}$ , where m has a value of from 2 to 8
- 5 c)  $-OC^*H(CH_3)CO_2C_mH_{2m+1}$ , where m has a value of from 1 to 10
- d)  $-OC(=O)C^*H(CH_3)OC_mH_{2m+1}$ , where m has a value of from 1 to 10
- e)  $-OC(=O)C^*H(F)C_mH_{2m+1}$ , where m has a value of from 1 to 10
- f)  $-OCH_2C^*H(F)C_mH_{2m+1}$ , where m has a value of from 1 to 10
- g)  $-OCH_2C^*H(F)C^*H(F)C_mH_{2m+1}$ , where m has a value of from 1 to
- 10 10
- h) oxirane-2,3-diyl

in which C\* denotes the asymmetric carbon atom.

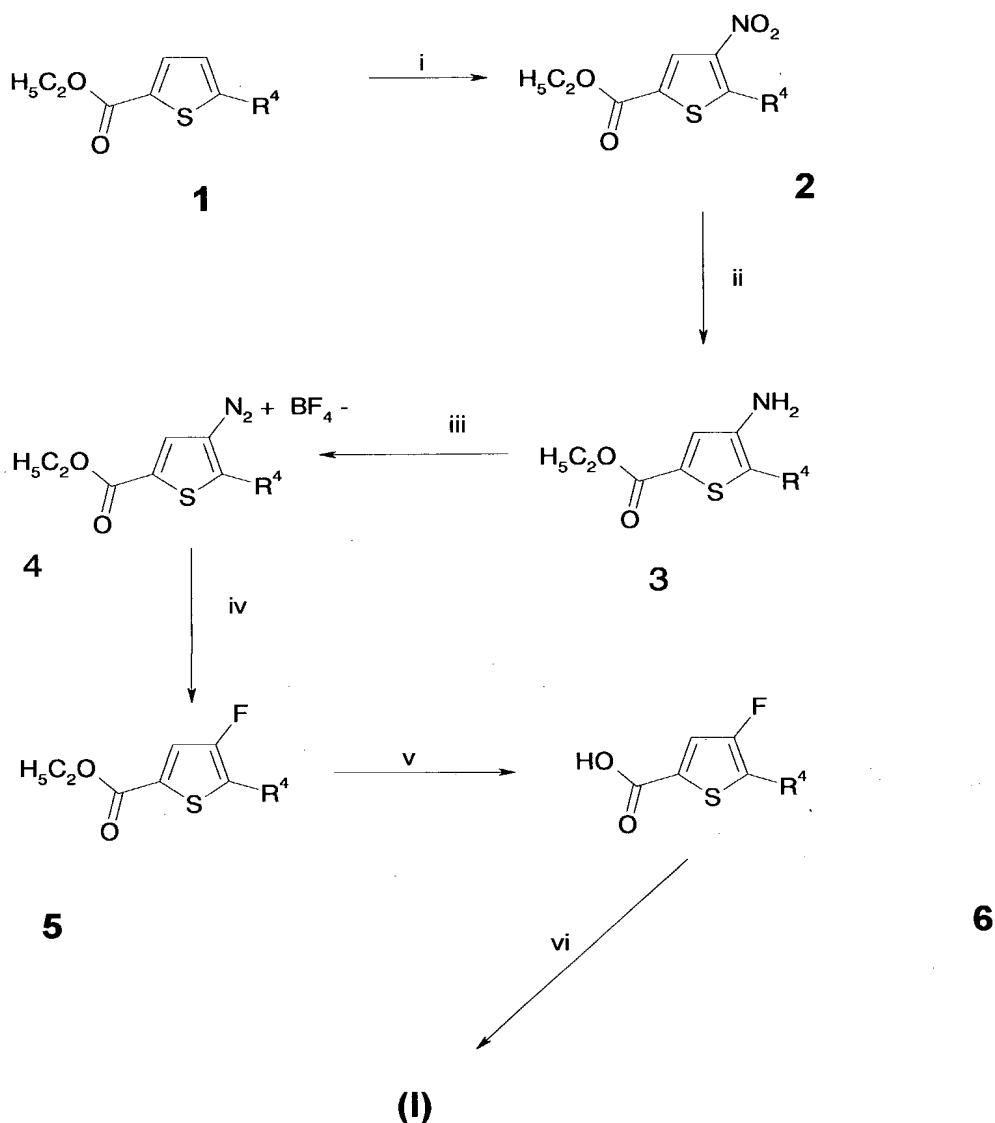
The compounds according to the invention are prepared by methods known per se  
15 from the literature, as described in standard works on organic synthesis, for example Houben-Weyl, Methoden der organischen Chemie [Methods of Organic Chemistry], Georg-Thieme-Verlag, Stuttgart.

However, it may prove necessary to vary or modify the literature methods for the  
20 requirements of mesogenic units, since, for example, functional derivatives having long ( $> C_6$ ) alkyl chains tend to be less reactive than, for example, the methyl or ethyl analogues.

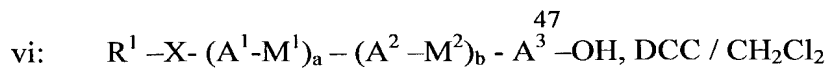
Particular reference is made in this connection to the following synthesis schemes  
25 for thiophene derivatives (i), in which the synthesis of the thiophene derivatives of the invention is illustrated in more detail by way of example.



Scheme 1



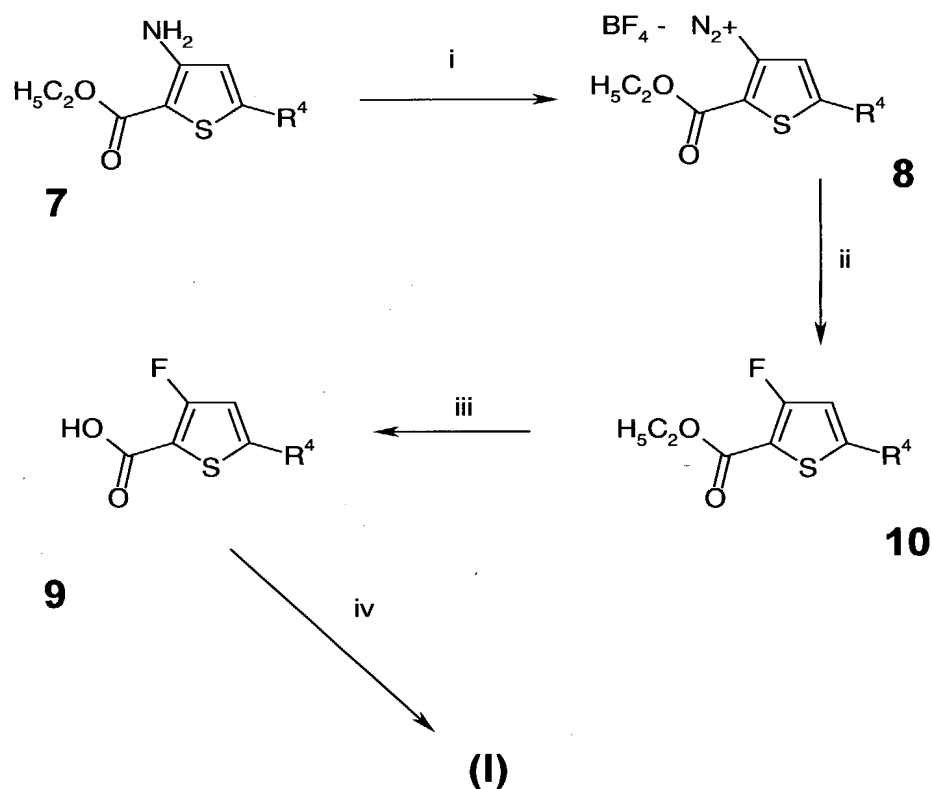
- 5 i:  $HNO_3$ ,  $H_2SO_4$  as described by Campaigne, J.Am.Chem.Soc. 73, 3812 (1951).
- ii:  $Sn$ ,  $HCl$  as described by Dewar, J.Am.Chem.Soc. 84, 3782 (1962)
- iii: 1.  $NaNO_2$  2.  $HBF_4$  as described by Corral, Heterocycles 23, 1431 (1985)
- iv: Thermolysis as described by Corral, Heterocycles 23, 1431 (1985)
- 10 v: 1.  $NaOH$ ,  $EtOH$  2.  $H^+$  as described by Corral, Heterocycles 23, 1431 (1985)



The 5-alkylthiophene-2-carboxylic esters **1** required for the synthesis in accordance with Scheme 1 are prepared as described in EP-B 0 500 072.

5

### Scheme 2

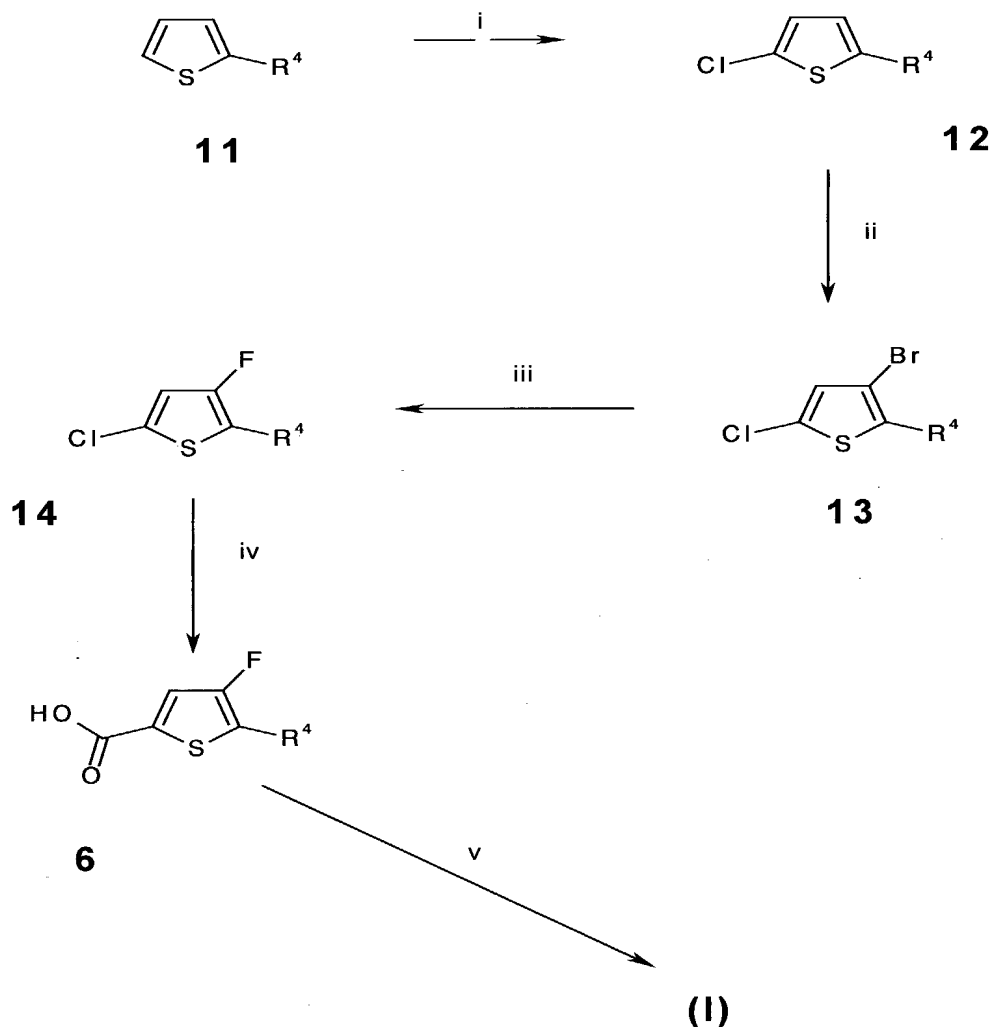


- 10 i: 1.  $NaNO_2$  2.  $HBF_4$  as described by Corral, Heterocycles 23, 1431 (1985)
- ii: Thermolysis as described by Corral, Heterocycles 23, 1431 (1985)
- iii: 1.  $NaOH$ ,  $EtOH$  2.  $H^+$  as described by Corral, Heterocycles 23, 1431 (1985)
- iv:  $R^1-X-(A^1-M^1)_a-(A^2-M^2)_b-A^3-OH$ , DCC /  $CH_2Cl_2$

15

The 5-alkyl-3-amino-thiophene-2-carboxylic esters **7** required for the synthesis in accordance with Scheme 2 are prepared as described by Huddleston, Synth. Commun. 9, 731 (1979) or in JP-A 05117263 or JP-A 06025221.

5 **Scheme 3**

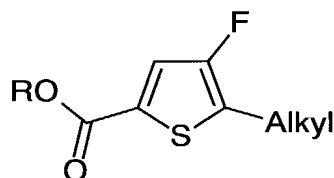


- i: N-chlorosuccinimide, HOAc, benzene as described by Lucas, Tetrahedron Lett. 40, 1775 (1999)
- ii: Br<sub>2</sub>, CHCl<sub>3</sub> as described by Lucas, Tetrahedron Lett. 40, 1775 (1999)
- iii: 1. BuLi 2. F-TEDA-BF<sub>4</sub>; step 1 as described by Lucas, Tetrahedron Lett. 40, 1775 (1999)

iv: 1. BuLi 2. CO<sub>2</sub> as described by Lucas, Tetrahedron Lett. 40, 1775 (1999)

v:  $R^1-X-(A^1-M^1)_a-(A^2-M^2)_b-A^3-OH$ , DCC / CH<sub>2</sub>Cl<sub>2</sub>

The invention furthermore provides the intermediate 5-alkyl-4-fluoro-thiophene-2-  
5 carboxylic acids of the formula (II)

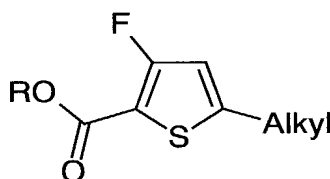


(II)

10 in which alkyl is a straight-chain or branched alkyl radical of 2 to 16 carbon atoms  
and R is hydrogen, alkali metal, alkaline earth metal (1/2), a straight-chain or  
branched alkyl radical of 1 to 16 atoms with the exception of methyl and tert-  
butyl, and

5-alkyl-3-fluoro-thiophene-2-carboxylic acids of the formula (III)

15



(III)

in which alkyl is a straight-chain or branched alkyl radical of 2 to 16 carbon atoms  
20 and R is hydrogen, alkali metal, alkaline earth metal (1/2), a straight-chain or  
branched alkyl radical of 1 to 16 atoms and corresponding acid halides, in  
particular acid chlorides, thereof.

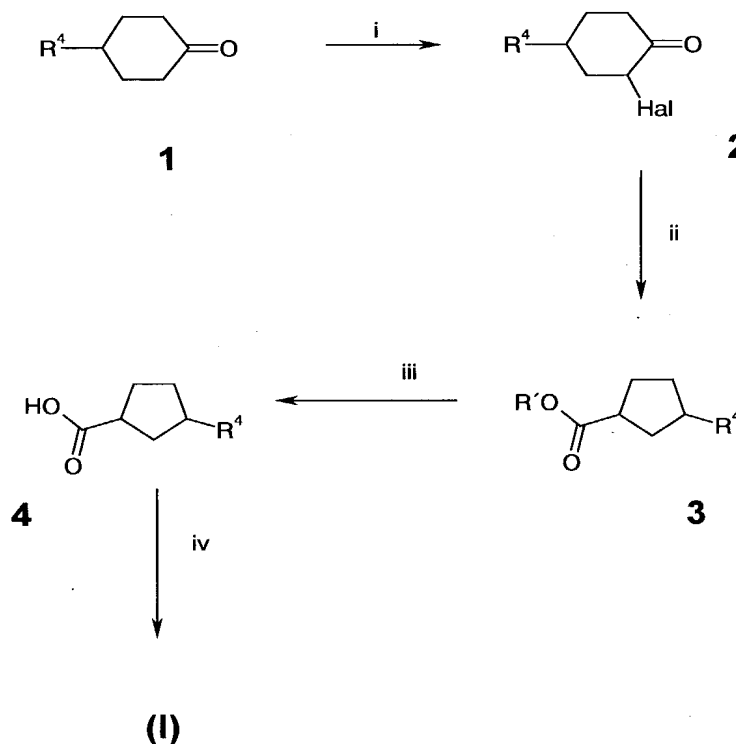
Some of them correspond to the abovementioned compounds of the formulae 5, 6,  
25 9 and 10. They can be used for preparing liquid crystals, agrochemicals and  
pharmaceuticals.

The 2-alkylthiophenes **11** required for the synthesis in accordance with Scheme 3 can be obtained as described in EP-B 0 500 072.

- 5 In this context, in particular for cyclopentane derivatives, reference is made to the synthesis schemes below in which the synthesis of the cyclopentane derivatives according to the invention is illustrated in more detail by way of example.

### Scheme 1

10



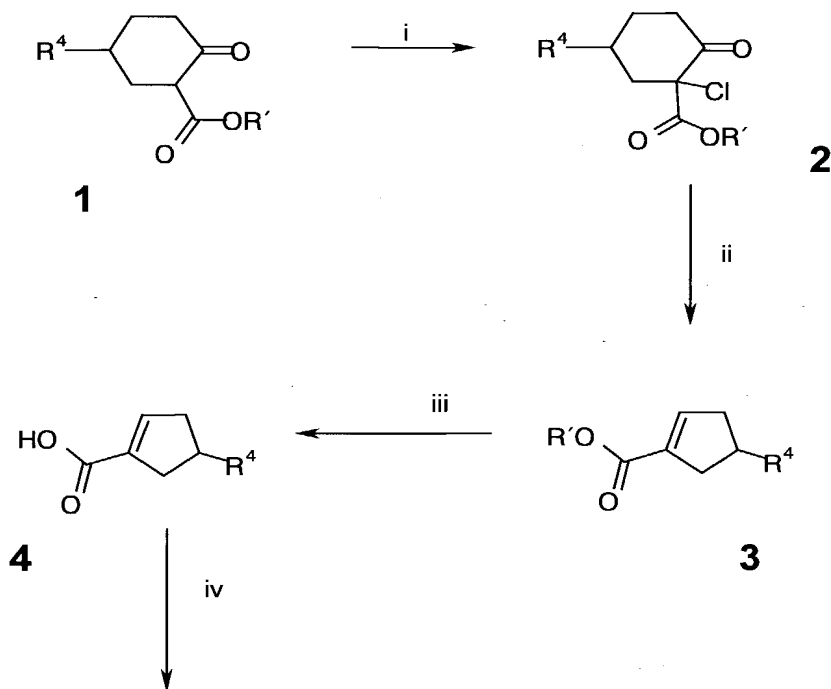
- i: N-bromosuccinimide,  $\text{CCl}_4$  as described by Corey, *J. Am. Chem. Soc.* 75, 2301 (1953).
- 15 ii:  $\text{NaOCH}_3$ , tert-butyl methyl ether as described in *Organic Syntheses, Coll. Vol. IV*, 594
- iii: 1.  $\text{NaOH} / \text{H}_2\text{O}$  2.  $\text{HCl}$
- iv:  $\text{R}^1 - \text{X} - (\text{A}^1 - \text{M}^1)_a - (\text{A}^2 - \text{M}^2)_b - \text{A}^3 - \text{OH}$ ,  $\text{DCC} / \text{CH}_2\text{Cl}_2$

If desired, this sequence may include an isomerization step to form the trans compounds, for example as described in US 4,873,019 (Example 3), at an appropriate point (for example using 4).

- 5 In this context, in particular for cyclopentene derivatives, reference is made to the synthesis schemes below in which the synthesis of the cyclopentene derivatives according to the invention is illustrated in more detail by way of example.

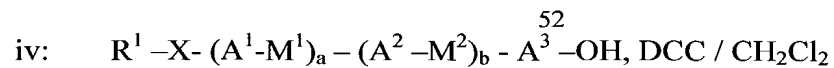
### Scheme 1

10



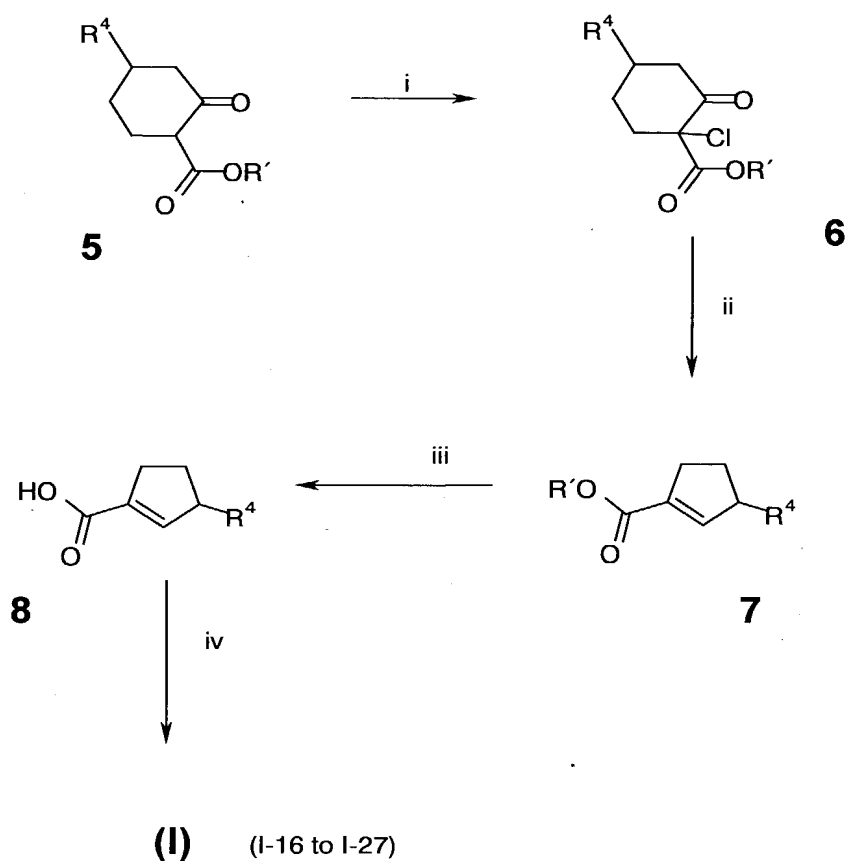
(I) (I-1 to I-12)

- i:  $t\text{-BuOCl}$ ,  $\text{CH}_3\text{OH}$  as described by Takeda, *Bull.Chem.Soc.Jpn.* 50(7), 1831 (1977).
- 15 ii:  $\text{Na}_2\text{CO}_3$ , xylene,  $160^\circ\text{C}$  as described by Takeda, *Bull.Chem.Soc.Jpn.* 50(7), 1831 (1977).
- iii: 1.  $\text{NaOH}/\text{H}_2\text{O}$  2.  $\text{HCl}$



## Scheme 2

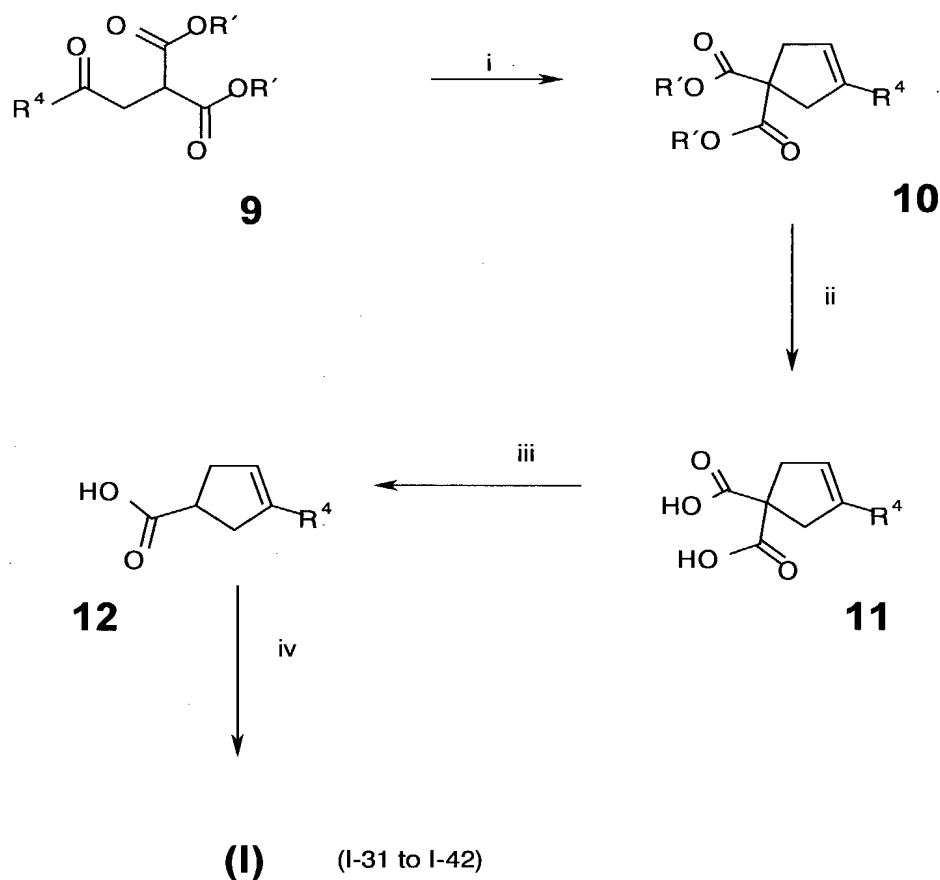
5



- i:  $t\text{-BuOCl}$ ,  $CH_3OH$  as described by Takeda, *Bull.Chem.Soc.Jpn.* 50(7), 1831 (1977).
- 10 ii:  $Na_2CO_3$ , xylene,  $160^\circ C$  as described by Takeda, *Bull.Chem.Soc.Jpn.* 50(7), 1831 (1977).
- iii: 1.  $NaOH/H_2O$  2.  $HCl$
- iv:  $R^1-X-(A^1-M^1)_a-(A^2-M^2)_b-A^3-OH$ , DCC /  $CH_2Cl_2$

The starting materials **1** and **5** required for the syntheses in accordance with schemes 1 and 2, respectively, can be prepared as described by Eisenbraun et al., J.Org.Chem. 32, 3010 (1967).

5

**Scheme 3**

- 10 i: Vinyltriphenylphosphonium bromide (Schweizer's Reagent), NaH, Et<sub>2</sub>O as described by Schweizer, *J.Org.Chem.* 30, 2082 (1965).
- ii: 1.KOH 2.HCl as described by Schweizer, *J.Org.Chem.* 30, 2082 (1965).
- iii: Thermolysis as described by Schweizer, *J.Org.Chem.* 30, 2082 (1965).
- iv: R<sup>1</sup>-X- (A<sup>1</sup>-M<sup>1</sup>)<sub>a</sub> - (A<sup>2</sup>-M<sup>2</sup>)<sub>b</sub> - A<sup>3</sup>-OH, DCC / CH<sub>2</sub>Cl<sub>2</sub>

15



The starting materials **9** required for the synthesis in accordance with Scheme 3 can be prepared as described by Hurd et al., J.Am.Chem.Soc. 70, 1650 (1948).

As far as the linking of functional derivatives of the furans, isoxazoles, thiazoles, cyclopentanes, cyclopentenones and fluorinated thiophenes with other liquid-crystal-specific units is concerned, express reference is made to DE-A 197 48 432, which gives a list of methods customary to the person skilled in the art.

The invention furthermore provides the use of compounds of the formula (I) in liquid-crystal mixtures, preferably smectic and nematic liquid-crystal mixtures, particularly preferably chiral smectic (ferroelectric) liquid-crystal mixtures. Particular preference is given to the use in ferroelectric liquid-crystal mixtures operated in inverse mode or in displays comprising active matrix elements. Very particular preference is given to the use in mixtures for active matrix LCDs in which the chiral smectic liquid-crystal layer forms a monostable monodomain.

The invention furthermore provides liquid-crystal mixtures, preferably smectic and nematic liquid-crystal mixtures, particularly preferably ferroelectric (chiral smectic) liquid-crystal mixtures, which comprise one or more compounds of the formula (I).

The liquid-crystal mixtures according to the invention generally comprise from 2 to 35 components, preferably from 2 to 25 components, particularly preferably from 2 to 20 components.

They generally comprise from 0.01 to 80% by weight, preferably from 0.1 to 60% by weight, particularly preferably from 0.1 to 30% by weight, based on the entire mixture, of one or more, preferably from 1 to 10, particularly preferably from 1 to 5, very particularly preferably from 1 to 3, compounds of the formula (I) according to the invention.

Further components of liquid-crystal mixtures which comprise compounds of the formula (I) according to the invention are preferably selected from known compounds having smectic and/or nematic and/or cholesteric phases. Further mixture components which are suitable in this context are listed, in particular, in international patent application PCT/EP96/03154 and in DE-A 197 48 432, which are incorporated herein by reference.

The mixtures according to the invention can in turn be used in electro-optical or fully optical elements, for example display elements, switching elements, light modulators, elements for image processing and/or signal processing, or generally in the area of nonlinear optics.

The invention therefore furthermore provides a switching and/or display device containing a liquid-crystal mixture, preferably a smectic liquid-crystal mixture, which comprises one or more compounds of the formula (I).

Particular preference is given to ferroelectric switching and/or display devices comprising active matrix elements (cf. e.g. DE-A 198 22 830).

The present application cites various documents, for example in order to illustrate the technical background to the invention. All these documents are incorporated herein by reference.

The examples which follow illustrate the invention.

### **Thiophene derivatives**

#### **Example 1**

**4-(5-Undecyl-pyrimidin-2-yl)phenyl**                      **4-fluoro-5-propyl-thiophene-2-carboxylate**

4.9 g of 4-(5-undecyl-pyrimidin-2-yl)phenol, 2.0 g of 4-fluoro-5-propyl-thiophene-2-carboxylic acid (prepared in accordance with Scheme 1 by nitrating methyl

5-propyl-thiophene-2-carboxylate in  $\text{HNO}_3/\text{H}_2\text{SO}_4$  to form methyl 4-nitro-5-propyl-thiophene-2-carboxylate, followed by reduction of the latter by means of  $\text{Sn} / \text{HCl}$  to give the corresponding amino compound, conversion of the latter into the diazonium tetrafluoroborate, thermolysis and, finally, hydrolysis) and 2.1 g of dicyclohexylcarbodiimide are stirred for 24 h in 50 ml of dichloromethane at room temperature. Filtration, removal of the dichloromethane by distillation, purification by chromatography (silica gel; dichloromethane / heptane) and recrystallization from acetonitrile affords the target compound as colorless crystals.

10

The compounds (I-1) to (I-12) can be obtained in a similar manner, and the compounds (I-17) to (I-29) can be obtained in a similar manner using the 5-alkyl-3-fluoro-thiophene-2-carboxylic acids prepared in accordance with Scheme 2.

15

**Example 2****(4-Fluoro-5-propyl-thiophen-2-yl)methyl 4-(5-undecyl-pyrimidin-2-yl)phenyl ether**

A fully reacted mixture of equimolar amounts of diethyl azodicarboxylate and triphenylphosphine in THF is admixed with equimolar amounts of 4-(5-undecyl-pyrimidin-2-yl)phenol and 4-fluoro-5-propyl-thiophen-2-yl-methanol (prepared by  $\text{LiAlH}_4$  reduction of methyl 4-fluoro-5-propyl-thiophene-2-carboxylate). After 24 h at room temperature the mixture is evaporated to dryness under reduced pressure. Purification by chromatography (silica gel, dichloromethane) and recrystallization affords the target compound.

25

The compounds (I-13) to (I-15) and (I-30) to (I-32) can be obtained in a similar manner.

The compounds of the formulae (I-16) and (I-33) can be obtained via the sequence 4-(or 3-)fluoro-5-alkyl-thiophen-2-yl-methanol -- 2-bromomethyl-4-(or 3-)fluoro-5-alkyl-thiophene -- 2-bromomethyl-5-alkyl-4-(or 3-)fluoro-thiophen-2-yl-

30

triphenylphosphonium salt -- Wittig reaction with 4-(5-R<sup>3</sup>-pyrimidin-2-yl)benzaldehyde -- hydrogenation.

### **Furan derivatives**

5

#### **Example 1**

##### **4-(5-Undecyl-pyrimidin-2-yl)phenyl 5-ethyl-furan-2-carboxylate**

4.9 g of 4-(5-undecyl-pyrimidin-2-yl)phenol, 1.4 g of 5-ethyl-2-furancarboxylic acid (prepared as described by Perry et al., Appl.Organomet.Chem. 10, 389-392 (1996) from furan-2-carboxylic acid; m.p. 90°C) and 2.1 g of  
10 dicyclohexylcarbodiimide are stirred for 24 h in 50 ml of dichloromethane at room temperature. Filtration, removal of the dichloromethane by distillation, purification by chromatography (silica gel; dichloromethane / heptane) and recrystallization from acetonitrile affords the target compound as colorless crystals  
15 having the phase sequence X 80 (N62) I.

The following compound is prepared in a similar manner

#### **Example 2**

20 **2-Fluoro-4-(5-undecyl-pyridin-2-yl)phenyl 5-ethyl-furan-2-carboxylate**  
which has a melting point of 76°C.

The compounds (I-1) to (I-12) can be prepared similarly to Example 1.

#### **Example 3**

##### **(5-Ethyl-furan-2-yl)methyl 4-(5-undecyl-pyrimidin-2-yl)phenyl ether**

A fully reacted mixture of equimolar amounts of diethyl azodicarboxylate and triphenylphosphine in THF is admixed with equimolar amounts of 4.9 g of 4-(5-undecyl-pyrimidin-2-yl)phenol and 5-ethyl-furan-2-yl-methanol (prepared by  
30 LiAlH<sub>4</sub> reduction of methyl 5-ethyl-furan-2-carboxylate, which in turn can be obtained by esterification of 5-ethyl-furan-2-carboxylic acid from Example 1). The mixture is stirred for 24 h at room temperature and then evaporated to dryness

under reduced pressure. Purification by chromatography (silica gel, dichloromethane) and recrystallization affords the target compound.

The compounds (I-13) to (I-15) can be obtained in a similar manner.

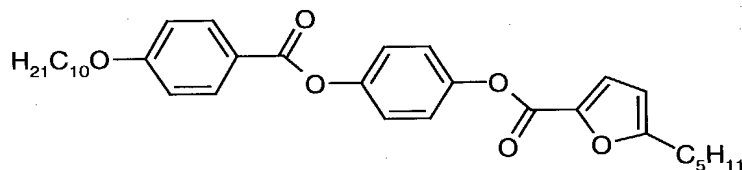
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The compounds of the formula (I-16) can be obtained via the sequence 5-ethyl-furan-2-yl-methanol -- 2-bromomethyl-5-ethyl-furan --2-bromomethyl-5-ethyl-furan-triphenylphosphonium salt -- Wittig reaction with 4-(5-R<sup>3</sup>-pyrimidin-2-yl)benzaldehyde -- hydrogenation.

10

The following compounds were obtained in a similar manner:

#### **Example 4**



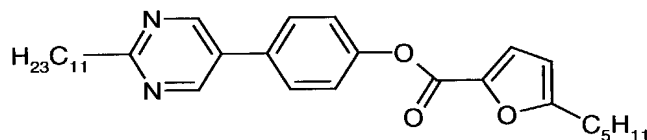
15

X 95 (N 92) I

4-(4-Decyloxy-benzoyloxy)phenyl 5-pentylfuran-2-carboxylate

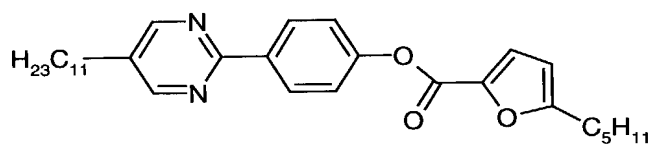
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#### **Example 5**

X 87 (S<sub>A</sub> 86) I

25

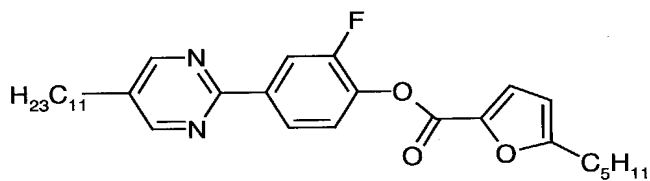
4-(2-Undecyl-pyrimidin-5-yl)phenyl 5-pentylfuran-2-carboxylate

**Example 6**

X 79 I

5

4-(5-Undecyl-pyrimidin-2-yl)phenyl 5-pentylfuran-2-carboxylate

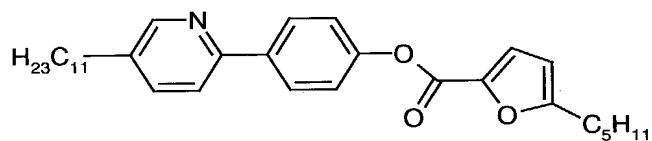
**Example 7**

10

X 83 I

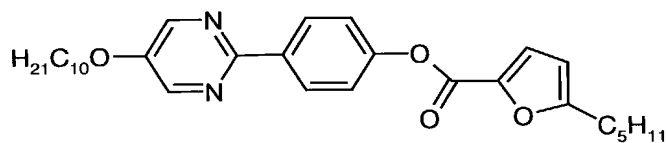
2-Fluoro-4-(5-undecyl-pyrimidin-2-yl)phenyl 5-pentylfuran-2-carboxylate

15

**Example 8**X 88 (S<sub>A</sub> 68 N 69) I

20

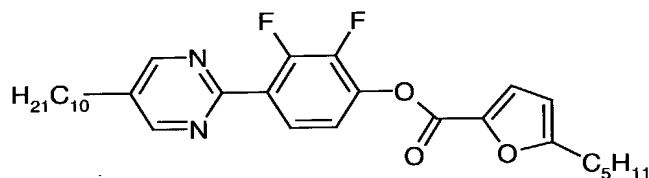
4-(5-Undecyl-pyridin-2-yl)phenyl 5-pentylfuran-2-carboxylate

**Example 9**

X 90 (N 90) I

5

4-(5-Decyloxy-pyrimidin-2-yl)phenyl 5-pentylfuran-2-carboxylate

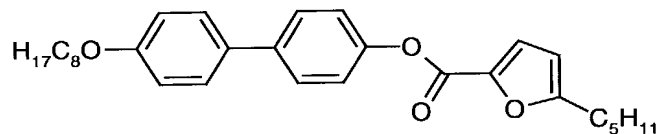
**Example 10**

10

X 67 I

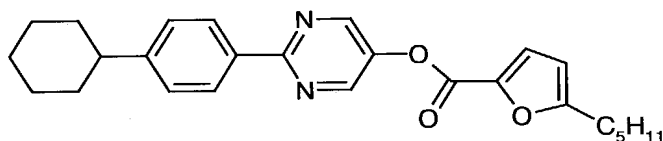
2,3-Difluoro-4-(5-decyl-pyrimidin-2-yl)phenyl 5-pentylfuran-2-carboxylate

15

**Example 11**X 78 S<sub>C</sub> 94 S<sub>A</sub> 96 I

20

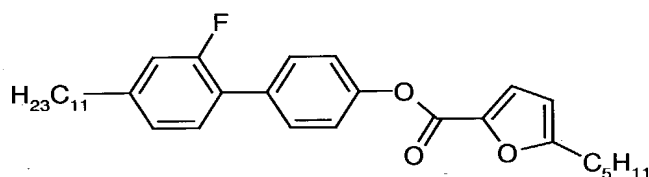
4-(4-Octyloxyphenyl)phenyl 5-pentylfuran-2-carboxylate

**Example 12**

X 142 I

5

2-(4-Cyclohexylphenyl)pyrimidin-5-yl 5-pentylfuran-2-carboxylate

**Example 13**

10

X 74 I

4-(2-Fluoro-4-undecyl-phenyl)phenyl 5-pentylfuran-2-carboxylate

**15 Isoxazole derivatives****Example 1****4-(5-Undecyl-pyrimidin-2-yl)phenyl 3-propyloxy-isoxazole-5-carboxylate**

4.9 g of 4-(5-undecyl-pyrimidin-2-yl)phenol, 1.7 g of 3-propyloxy-isoxazole-5-carboxylic acid (prepared as described by Xue et al., Bioorg.Med.Chem.Letters 8 (1998) 3499 by reacting methyl 3-hydroxy-isoxazole-5-carboxylate, which is commercially available, with 1-bromopropane at 60°C in dimethylformamide / potassium carbonate followed by hydrolysis with LiOH in tetrahydrofuran) and 2.1 g of dicyclohexylcarbodiimide are stirred for 24 h in 50 ml of dichloromethane at room temperature. Filtration, removal of the dichloromethane by distillation, purification by chromatography (silica gel; dichloromethane / heptane) and



recrystallization from acetonitrile affords the target compound as colorless crystals having the phase sequence X 91 S<sub>A</sub> 109 N 126 I.

The compounds (I-1) to (I-12) in which R<sup>4</sup> is an alkoxy radical can be prepared similarly to Example 1, and the compounds (I-1) to (I-12) in which R<sup>4</sup> is an alkyl radical can likewise be prepared using 3-alkyl-isoxazole-5-carboxylic acids prepared as described by Dulin et al., Proc.Soc.exp.Biol.Med., 1966, 121, 777.

### **Example 2**

#### **(3-Propyloxy-isoxazol-5-yl)methyl 4-(5-undecyl-pyrimidin-2-yl)phenyl ether**

A fully reacted mixture of equimolar amounts of diethyl azodicarboxylate and triphenylphosphine in THF is admixed with equimolar amounts of 4-(5-undecyl-pyrimidin-2-yl)phenol and 3-propyloxy-isoxazol-5-yl-methanol (prepared by LiAlH<sub>4</sub> reduction of methyl 3-propyloxy-isoxazole-5-carboxylate). The mixture is stirred for 24 h at room temperature and then evaporated to dryness under reduced pressure. Purification by chromatography (silica gel, dichloromethane) and recrystallization affords the target compound.

The compounds (I-13) to (I-15) can be prepared in a similar manner.

### **Thiazole derivatives**

#### **Example 1**

#### **[4-(5-Undecyl-pyrimidin-2-yl)phenyl] 2-propyl-thiazole-5-carboxylate**

4.9 g of 4-(5-undecyl-pyrimidin-2-yl)phenol, 1.7 g of 2-propyl-thiazole-5-carboxylic acid (prepared as described by Clemence et al., Eur.J.Med.Chem.-Chimica Therapeutica 1976-11, no.6, p.567-570) and 2.1 g of dicyclohexylcarbodiimide are stirred for 24 h in 50 ml of dichloromethane at room temperature. Filtration, removal of the dichloromethane by distillation, purification by chromatography (silica gel; dichloromethane / heptane) and recrystallization from acetonitrile affords the target compound as colorless crystals.

The compounds (I-1) to (I-12) can be prepared in a similar manner to Example 1.

### **Example 2**

#### **5 (2-Propyl-thiazol-5-yl)methyl 4-(5-undecyl-pyrimidin-2-yl)phenyl ether**

A fully reacted mixture of equimolar amounts of diethyl azodicarboxylate and triphenylphosphine in THF is admixed with equimolar amounts of 4-(5-undecyl-pyrimidin-2-yl)phenol and 2-propylthiazol-5-yl-methanol (prepared by  $\text{LiAlH}_4$  reduction of methyl 2-propylthiazole-5-carboxylate). The mixture is stirred for 24  
10 h at room temperature and then evaporated to dryness under reduced pressure. Purification by chromatography (silica gel, dichloromethane) and recrystallization affords the target compound.

The compounds (I-13) to (I-15) can be obtained in a similar manner.

15

### **Cyclopentane derivatives**

#### **Example 1**

#### **4-(5-Undecyl-pyrimidin-2-yl)phenyl 3-ethyl-cyclopentanecarboxylate**

20 4.9 g of 4-(5-undecyl-pyrimidin-2-yl)phenol, 1.5 g of 3-ethyl-cyclopentane-carboxylic acid and 2.1 g of dicyclohexylcarbodiimide are stirred for 24 h in 50 ml of dichloromethane at room temperature. Filtration, removal of the dichloromethane by distillation, purification by chromatography (silica gel; dichloromethane / heptane) and recrystallization from acetonitrile affords the  
25 target compound as colorless crystals.

The compounds (I-1) to (I-12) can be obtained in a similar manner.

### **Example 2**

#### **30 4-(5-Undecyl-pyrimidin-2-yl)phenyl (3-ethyl-cyclopentan-1-yl)methyl ether**

A fully reacted mixture of equimolar amounts of diethyl azodicarboxylate and triphenylphosphine in THF is admixed with equimolar amounts of 4-(5-undecyl-

pyrimidin-2-yl)phenol and 3-ethyl-cyclopentan-1-yl-methanol (prepared by LiAlH<sub>4</sub> reduction of methyl 3-ethyl-cyclopentanecarboxylic acid). The mixture is stirred for 24 h at room temperature and then evaporated to dryness under reduced pressure. Purification by chromatography (silica gel, dichloromethane) and  
5 recrystallization affords the target compound.

The compounds (I-13) to (I-15) can be obtained in a similar manner.

The compounds of the formulae (I-16) and (I-33) can be obtained via the sequence

10 *3-alkyl-cyclopentan-1-yl-methanol*

*1-bromomethyl-3-alkyl-cyclopentane*

*(1-bromomethyl-3-alkyl-cyclopentane)triphenylphosphonium salt*

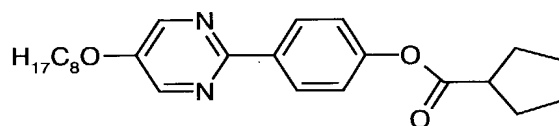
*Wittig reaction with 4-(5-R<sup>3</sup>-pyrimidin-2-yl)benzaldehyde*

*hydrogenation*

15

The following compounds were obtained in a similar manner:

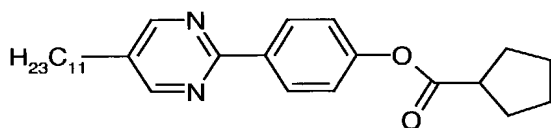
### **Example 3**



20

X 95 I

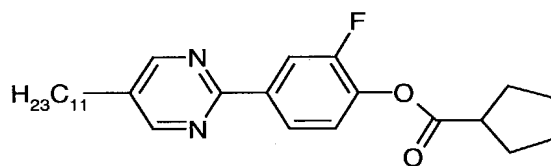
4-(5-Octyloxy-pyrimidin-2-yl)phenyl cyclopentanecarboxylate

**Example 4**

X 73 I

5

4-(5-Undecyl-pyrimidin-2-yl)phenyl cyclopentanecarboxylate

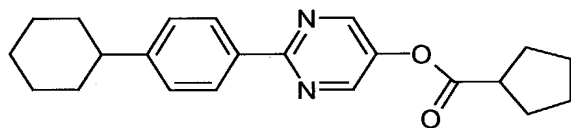
**Example 5**

X 66 I

10

2-Fluoro-4-(5-undecyl-pyrimidin-2-yl)phenyl cyclopentanecarboxylate

15

**Example 6**

X 164 I

20

2-(4-Cyclohexyl)phenyl-pyrimidin-5-yl cyclopentanecarboxylate

**Cyclopentene derivatives****Example 1**

25

**4-(5-Undecyl-pyrimidin-2-yl)phenyl 3-ethyl-1-cyclopentene-1-carboxylate**

4.9 g of 4-(5-undecyl-pyrimidin-2-yl)phenol, 1.5 g of 3-ethyl-1-cyclopentene-1-carboxylic acid and 2.1 g of dicyclohexylcarbodiimide are stirred for 24 h in 50 ml

of dichloromethane at room temperature. Filtration, removal of the dichloromethane by distillation, purification by chromatography (silica gel; dichloromethane / heptane) and recrystallization from acetonitrile affords the target compound.

5

The compounds (I-1) to (I-12), (I-16) to (I-27) and (I-31) to (I-42) can be obtained in a similar manner.

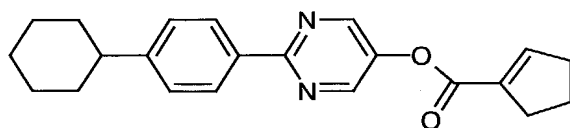
### **Example 2**

#### **10 (3-Ethyl-1-cyclopenten-1-yl)methyl 4-(5-undecyl-pyrimidin-2-yl)phenyl ether**

A fully reacted mixture of equimolar amounts of diethyl azodicarboxylate and triphenylphosphine in THF is admixed with equimolar amounts of 4-(5-undecyl-pyrimidin-2-yl)phenol and 3-ethyl-1-cyclopenten-1-yl-methanol (prepared by LiAlH<sub>4</sub> reduction of methyl 3-ethyl-1-cyclopentene-1-carboxylate as described by  
15 Takeda, Bull.Chem.Soc.Jpn. 50 (7),1831 (1977)). The mixture is stirred for 24 h at room temperature and then evaporated to dryness under reduced pressure. Purification by chromatography (silica gel, dichloromethane) and recrystallization affords the target compound.

20 The compounds (I-13) to (I-15), (I-28) to (I-30) and (I-43) to (I-45) can be obtained in a similar manner.

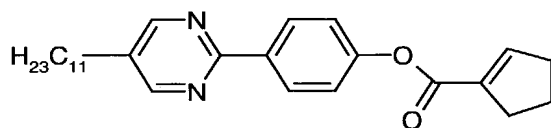
The following compounds were obtained in a similar manner:

**Example 3**

X 176 I

5

2-(4-Cyclohexyl)phenyl-pyrimidin-5-yl cyclopent-1-ene-1-carboxylate

**Example 4**

10

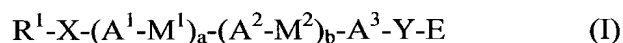
X 109 I

4-(5-Undecyl-pyrimidin-2-yl)phenyl cyclopent-1-ene-1-carboxylate

**Patent claims**

5

1. A five-membered ring compound of the formula (I),



10 where the symbols and indices have the following meanings:

**E** is a radical **T-Z-R<sup>2</sup>** containing a five-membered ring, where:

- (i) **T** is undirected and is
- 15 4-fluorothiophene-2,5-diyl, 3-fluorothiophene-2,5-diyl,  
3-fluorothiophene-2,4-diyl or 5-fluorothiophene-2,4-diyl
- Z** is a single bond or -O-
- R<sup>2</sup>** is hydrogen or a straight-chain or branched alkyl radical (with or  
without asymmetric carbon atoms) having 1 to 20 carbon atoms,  
20 where one nonterminal CH<sub>2</sub> group may be replaced by -O- or  
-OC(=O)- or -C(=O)O- and/or one or more H atoms may be  
replaced by F, with the provisos that
- b) the -CH<sub>2</sub>- group nearest to the thiophene cannot be replaced by  
-O- when Z is -O-
- 25 b) R<sup>2</sup> can only be hydrogen when Z is a single bond,
- (ii) **T** is furan-2,5-diyl or furan-2,4-diyl
- Z** is a single bond or -O-
- 30 **R<sup>2</sup>** is hydrogen or a straight-chain or branched alkyl radical (with or  
without asymmetric carbon atoms) having 1 to 20 carbon atoms,  
where one nonterminal CH<sub>2</sub> group nonadjacent to furan may be

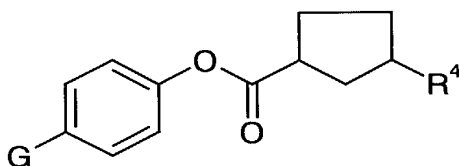
replaced by -O- or -OC(=O)- or -C(=O)O- and/or one or more H atoms may be replaced by F,

- (iii) **T** is undirected and is isoxazole-3,5-diyl  
5 **Z** is a single bond or -O-
- R<sup>2</sup>** is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 20 carbon atoms, where one nonterminal CH<sub>2</sub> group may be replaced by -O- or -OC(=O)- or -C(=O)O- and/or one or more H atoms may be replaced by F, with the provisos that  
10 a) the -CH<sub>2</sub>- group nearest to the isoxazole cannot be replaced by -O- when Z is -O-  
b) R<sup>2</sup> can only be hydrogen when Z is a single bond,
- 15 (iv) **T** is undirected and is thiazole-2,5-diyl or thiazole-2,4-diyl  
**Z** is a single bond  
**R<sup>2</sup>** is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 20 carbon atoms, where one nonterminal CH<sub>2</sub> group may be replaced by -O- or -OC(=O)- or -C(=O)O- and/or one or more H atoms may be replaced by F,  
20
- (v) **T** is cyclopentane-1,3-diyl  
25 **Z** is a single bond or -O-  
**R<sup>2</sup>** is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 20 carbon atoms, where one nonterminal CH<sub>2</sub> group may be replaced by -O- or -OC(=O)- or -C(=O)O- and/or one or more H atoms may be replaced by F, with the provisos that  
30 a) the -CH<sub>2</sub>- group nearest to the cyclopentane cannot be replaced by -O- when Z is -O-



b)  $R^2$  can only be hydrogen when Z is a single bond,

with the exception of compounds of the formula (II)



(II)

in which

$R^4$  is as defined for  $R^2$

**G** is trans-4-propyl-cyclohexyl or trans-4-butyl-cyclohexyl or an alkyl group of 1 to 15 carbon atoms, in which, in addition, one or more nonadjacent  $CH_2$  groups may be replaced by -O-, -CO-, -OCO-, -O-CO-O-, -CHhalogen-, -CHCN- and/or -CH=CH- or is F, CN,

(vi) **T** is cyclopentane-1,3-diyl, in which one - $CH_2CH_2$ - or - $CH_2CH$ - group is replaced by a -CH=CH- or. CH=C- group respectively

**Z** is a single bond

**$R^2$**  is hydrogen or a straight-chain or branched alkyl radical (with or without asymmetric carbon atoms) having 1 to 20 carbon atoms, where one nonterminal  $CH_2$  group may be replaced by -O- or -OC(=O)- or -C(=O)O- and/or one or more H atoms may be replaced by F, with the proviso that the - $CH_2$ - group nearest to the cyclopentene cannot be replaced and where

**Y** cannot be - $CH_2-CH_2$ -,

25

**$R^1$**  is hydrogen or a straight-chain or branched  $C_{1-20}$ -alkyl or  $C_{2-20}$ -alkenyl radical (with or without asymmetric carbon atoms), where

- a) one or two nonterminal CH<sub>2</sub> groups may be replaced, independently of one another, by -O- or -C(=O)-, with the proviso that two adjacent CH<sub>2</sub> groups cannot be replaced in the same way, and/or
- b) one CH<sub>2</sub> group may be replaced by -C≡C-, and/or
- 5 c) one CH<sub>2</sub> group may be replaced by -Si(CH<sub>3</sub>)<sub>2</sub>-, cyclopropane-1,2-diyl, cyclobutane-1,3-diyl, cyclopentane-1,4-diyl, bicyclo[1.1.1]pentane-1,3-diyl or cyclohexane-1,4-diyl, and/or
- d) one or more H atoms may be replaced by F and/or CN,
- 10 e) in the case of a branched alkyl radical containing asymmetric carbon atoms, the asymmetric carbon atoms have -CH<sub>3</sub>, -OCH<sub>3</sub>, -CF<sub>3</sub>, F, CN and/or Cl as substituents or are incorporated into a 3- to 7-membered ring, in which, in addition, one or two non-adjacent CH<sub>2</sub> groups may be replaced by -O- and one CH<sub>2</sub> group non-adjacent to these groups may be replaced by -OC(=O)-;
- 15

**X** is a single bond, -O-, OC(=O)-, -C(=O)O- or -OC(=O)O-

**Y** is -OC(=O)-, -OCH<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>-

- 20 **A<sup>1</sup>, A<sup>2</sup>, A<sup>3</sup>** are each, independently of one another, phenylene-1,4-diyl, unsubstituted or monosubstituted or disubstituted by CN or F, phenylene-1,3-diyl, unsubstituted or monosubstituted or disubstituted by CN or F, cyclohexane-1,4-diyl, in which one or two H atoms may be replaced by CN and/or CH<sub>3</sub> and/or F, 1-cyclohexene-1,4-diyl, in
- 25 which one H atom may be replaced by F, 1-alkyl-1-silacyclohexane-1,4-diyl, pyridine-2,5-diyl, unsubstituted or monosubstituted by F, pyrimidine-2,5-diyl, unsubstituted or monosubstituted by F, cyclopentane-2,5-diyl or thiophene-2,5-diyl;

- 30 **M<sup>1</sup>, M<sup>2</sup>** are undirected and are each, independently of one another, -OC(=O)-, -OCH<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>-, -OC(=O)CH<sub>2</sub>CH<sub>2</sub>-, -OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-, -C≡C-, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>- or a single bond;

**a, b** are each, independently of one another, 0 or 1.

2. A liquid-crystal mixture comprising at least one compound of the formula (I) as claimed in claim 1.

5

3. A liquid-crystal mixture as claimed in claim 2, which comprises from 0.01 to 80% by weight of one or more compounds of the formula (I).

10

4. A liquid-crystal mixture as claimed in claim 2 or 3, which is ferroelectric (chiral smectic).

5. A liquid-crystal mixture as claimed in claim 2 or 3, which is nematic.

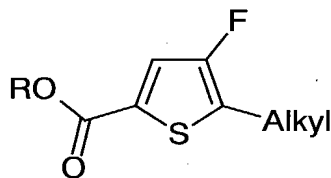
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6. A ferroelectric switching and/or display device, which contains a ferroelectric liquid-crystal mixture as claimed in claim 4.

7. A ferroelectric switching and/or display device as claimed in claim 6, which contains active matrix elements and wherein the liquid-crystal layer forms a monostable monodomain.

20

8. A 5-alkyl-4-fluoro-thiophene-2-carboxylic acid of the formula (II)

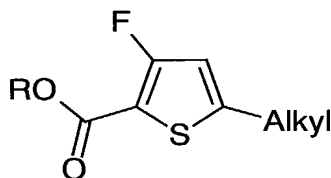


(II)

25

in which alkyl is a straight-chain or branched alkyl radical of 2 to 16 carbon atoms and R is hydrogen, alkali metal, alkaline earth metal (1/2), a straight-chain or branched alkyl radical of 1 to 16 atoms with the exception of methyl and tert-butyl, or a corresponding acid halide.

9. A 5-alkyl-3-fluoro-thiophene-2-carboxylic acid of the formula (III)



(III)

in which alkyl is a straight-chain or branched alkyl radical of 2 to 16 carbon atoms and R is hydrogen, alkali metal, alkaline earth metal (1/2), a straight-chain or branched alkyl radical of 1 to 16 atoms or a corresponding acid halide.

10. The use of compounds of the general formulae (II) and (III) as claimed in claims 8 and 9 for preparing liquid crystals, agrochemicals and pharmaceuticals.

11. A fluorinated five-membered ring compound as claimed in claim 1, wherein, in the cyclopentene derivatives (vi), T is 1-cyclopentene-1,3-diyl, 1-cyclopentene-1,4-diyl or 3-cyclopentene-1,3-diyl.

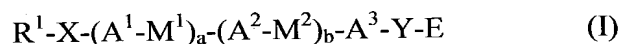
12. A fluorinated five-membered ring compound as claimed in claim 11, wherein, in the cyclopentene derivatives (vi), the moiety -Y-T- is

1-cyclopentene-1-carbonyloxy-3-yl, 1-cyclopentene-1-carbonyloxy-4-yl or 3-cyclopentene-1-carbonyloxy-3-yl.

**Abstract**

5

Fluorinated five-membered ring compounds of the formula (I)



10 where E is a radical T-Z-R<sup>2</sup> containing a five-membered ring and, for example,

T is undirected and is 4-fluorothiophene-2,5-diyl, 3-fluorothiophene-2,5-diyl,  
3-fluorothiophene-2,4-diyl, 5-fluorothiophene-2,4-diyl, furan-2,5-diyl,  
furan-2,4-diyl, isoxazole-3,5-diyl, thiazole-2,5-diyl, thiazole-2,4-diyl,  
15 cyclopentane-1,3-diyl or cyclopentene-1,3-diyl,

R<sup>1</sup> and R<sup>2</sup> are hydrogen,

X is a single bond, -O-, OC(=O)-, -C(=O)O- or -OC(=O)O-,

20 Y is -OC(=O)-, -OCH<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>-,

Z is a single bond or -O-,

A<sup>1</sup>, A<sup>2</sup>, A<sup>3</sup> are each, independently of one another, phenylene-1,4-diyl,

25 M<sup>1</sup>, M<sup>2</sup> are undirected and are each, independently of one another,

-OC(=O)-, -OCH<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>-, -OC(=O)CH<sub>2</sub>CH<sub>2</sub>-, -OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-,

-C≡C-, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>- or a single bond,

a, b are each, independently of one another, 0 or 1,

30

are used in FLC mixtures.

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**DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY**  
(Includes reference to PCT International Applications)

FROMMER LAWRENCE & HAUG, LLP  
File No.: 514453-3916

As a below named inventor, we hereby declare that:

Our residences, post office addresses and citizenships are as stated below next to our names.

We believe we are original, first and joint inventors (if plural, names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention ENTITLED:

**FIVE MEMBERED-RING COMPOUNDS AND UTILIZATION THEREOF IN LIQUID CRYSTAL MIXTURES**

the specification of which:

- is attached hereto
- X was filed on February 27, 2002 as:
- X United States Application Serial No. 10/070242
- X Corresponding to International Appln. No. **PCT/EP00/08518** filed **August 31, 2000** with amendments through DATE EVEN HEREWITH (if applicable, give details).

We hereby state that we have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to our to be material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

We hereby claim foreign priority benefits under Title 35, United States Code § 119 (a) - (d) or § 365 (b) of any foreign application(s) for patent or inventor's certificate, or § 365 (a) of any PCT International application(s) designating at least one country other than the United State of America listed below and have also identified below any foreign application for patent or inventor's certificate or any PCT International applications designating at least one country other than the United States of America filed by us on the same subject matter having a filing date before that of the application(s) on which priority is claimed: Prior Foreign/PCT Application(s) [list additional applications on separate page]:

Country (or PCT)	Application Number:	Filed (Day/Month/Year)	Priority Claimed:	
			Yes	No
Germany	199 41 649.4	September 1, 1999	x	
Germany	199 41 651.6	September 1, 1999	x	
Germany	199 41 650.8	September 1, 1999	x	
Germany	199 41 653.2	September 1, 1999	x	
Germany	199 41 654.0	September 1, 1999	x	
Germany	199 41 656.7	September 1, 1999	x	

We hereby claim the benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below.

We hereby claim the benefit under Title 35, United States Code § 120 of any United States application(s) or § 365 (c) of any PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior United States or PCT International application(s) in the manner provided by the first paragraph of Title 35, United States Code § 112, we acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to us to be material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

Prior U.S. (or U.S.-designating PCT) Application(s) [list additional applications on separate page]:

<u>U.S. Serial No.:</u>	<u>Filed (Day/Month/Year)</u>	<u>PCT Application No.</u>	<u>Status (patented, pending, abandoned)</u>
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✓ We hereby appoint William F. Lawrence, Registration No. 28,029, and FROMMER LAWRENCE & HAUG, LLP or their duly appointed associates, our attorneys or agents, with full power of substitution and revocation, to prosecute this application, to make alterations and amendments therein, to file continuation and divisional applications thereof, to receive the Patent, and to transact all business in the Patent and Trademark Office and in the Courts in connection therewith, and to insert the Serial

Number of the application in the space provided above, and specify that all communications about the application are to be directed to the following correspondence address:

William F. Lawrence, Esq.  
c/o FROMMER LAWRENCE &  
HAUG, LLP  
745 Fifth Avenue  
New York, NY 10151

Direct all telephone calls to: (212) 588-0800  
to the attention of:  
William F. Lawrence  
FAX (212) 588-0500

We hereby declare that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

## INVENTOR(S):

Signature:

Full name of first or sole inventor: Barbara HORNUNG

Residence: Schulstrasse 21 A, D-63594 Hasselroth, Germany DEX

Citizenship: Germany

Date: 07. OKT. 2002

Signature:

Full name of second inventor: Toshiaki NONAKA

Residence: Kubo 1-18-10 Kakegawa-shi, Shizuoka Pref. 436-0027, Japan JPX

Citizenship: Japan

Date: 2002.9.6

Signature:

Full name of third inventor: Ayako OGAWA

Residence: Shimomata minami 1-6-19-101 Kakegawa City, Shizuoka Pref. 436-0026, Japan JPX

Citizenship: Japan

Date: 2002.9.5

Signature:

Full name of fourth inventor: Wolfgang SCHMIDT

Residence: Staffordstrasse 5A, D-63303 Dreieich, Germany DEX

Citizenship: Germany

Date: 07. OKT. 2002

Signature:

Full name of fifth inventor: Rainer WÄGEN

Residence: Langenhainer Weg 11, D-65795 Hattersheim, Germany DEX

Citizenship: Germany

Date: 07. OKT. 2002

Post Office Address(es) of inventors [if different from residence]:

NOTE: In order to qualify for reduced fees available to Small Entities, each inventor and any other individual or entity having rights to the invention must also sign an appropriate separate "Verified Statement (Declaration) Claiming [or Supporting a Claim by Another for] Small Entity Status" form [e.g. for Independent Inventor, Small Business Concern, Nonprofit Organization, Individual Non-Inventor].